HEAT.

AN ELEMENTARY
TEXT-BOOK OF PHYSICS.

PART IV.

HEAT.

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With 84 Illustrations.

PREFACE.

THIS volume, which is issued as Part IV. of an Elementary Text-Book of Physics, deals with the elements of *Heat*. It is intended to give a simple exposition of the fundamental principles of the subject, and, at the same time, to give some insight into the theory and practice of the experimental methods by which these principles are established and illustrated.

The book has not been written specially to meet the requirements of any particular syllabus, but the treatment is sufficiently complete and general to meet the needs of students preparing for any of the usual elementary examinations in this subject.

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CONTENTS.

H E A T.

CHAPTER I.

INTRODUCTORY.

1. **Nature of Heat.**—We are familiar in everyday experience with the ordinary sensations of heat and cold. We are also familiar with the statements that as a body becomes hotter it gains heat, and as it becomes colder it loses heat. These statements, however, at once suggest a question as to the nature of that which is here called **heat.**

This question has been the subject of speculation and experimental research from the earliest times, and it was only during the first half of last century, between the years 1798 and 1848, that it was finally and satisfactorily answered. At first, heat was supposed to be a subtle fluid, called **caloric**, which was assumed to be able to permeate all matter. A body was supposed to become warmer as this fluid flowed into it, and colder as the fluid flowed out of it. The properties assigned to the fluid were such as were necessary to explain the familiar phenomena of heat, and, to meet the objection that a body does not change in weight when it gains or loses heat, the fluid was held, by most supporters of the caloric theory, to be without weight.

It is now known, mainly as the result of the experimental work of Count Rumford (Benjamin Thomson) and of Dr. Joule of Manchester, that heat is a form of energy.

It will be found, on investigation, that in all cases where heat is generated it is produced by the transformation of energy in some other form into heat. The most familiar source of heat is **combustion.** In this case **chemical energy** is transformed mainly into heat during the process of chemical combination known as combustion. Heat may also be produced by the expenditure of mechanical work ; for example, a metal button may be made extremely hot by rubbing it vigorously on a piece of wood, and a piece of soft iron may be heated by hammering it on an anvil. In these cases the mechanical work done against friction in rubbing the button on the wood, or against molecular forces in deforming the iron, is converted into heat.

Another important method of producing heat is by the conversion of electrical energy into heat. When an electric current is passed through any conductor, such as the filament in an ordinary incandescent lamp, the energy expended in maintaining the current through the conductor is transformed into heat in the conductor. In some cases the conductor may, as in the case of the incandescent lamp filament, be heated in this way to bright incandescence.

Heat is therefore held to be **a form of energy**, and there are good reasons for believing that it is the form of energy which a substance possesses in virtue of the vibratory motion of its molecules.

The molecules of a body are not packed together as motionless particles in close contact, but are supposed to be grouped closely together in dynamical equilibrium, each one being quite free and separate from the others, and maintained in rapid vibratory motion within the limits of the small space in which it is free to move. The total molecular **kinetic energy** which a body thus possesses in virtue of the vibratory motion of its molecules is the

heat which the body possesses. When a body is heated the energy of the vibratory motion of the molecules is increased, and when the body is cooled the energy of the vibratory motion of its molecules is decreased.

2. **Temperature.**—The thermal difference between two bodies which we usually express by saying that one body is **hotter** or **colder** than the other is a difference in **temperature**. Temperature is thus a term which applies to the degree of hotness of a body. As a body becomes hotter or colder its temperature changes; when the body becomes hotter its temperature is said to rise, and when it becomes colder its temperature is said to fall.

The term temperature thus applies to a particular thermal state of the body, and is, therefore, essentially distinct from the quantity of heat which the body possesses. Bodies differing widely in mass and material may, on account of these differences, possess very different quantities of the form of energy known as heat, but they may be all at exactly the same temperature. Thus, all the objects in a uniformly heated room are at the same temperature, but they possess very different quantities of heat.

It should be noticed that difference of temperature is the condition of transfer of heat from one body to another in contact with it, or from one point to another in the same body. Thus, when a kettle full of water is placed on the fire, it is heated, because heat passes from the hot fire to the colder kettle; similarly, if a piece of iron is placed in the fire, it is heated by the transfer of heat from the fire to the iron, until the latter finally attains the temperature of the fire at the point where it rests.

Two bodies may therefore be defined to be at the same temperature when their states are such that no heat passes from one to the other when they are placed in contact. The transfer of heat, by **radiation**, between bodies not in contact with each other is dealt with in a later chapter.

The sense of touch enables us to perceive differences of temperature. Thus, a substance at a temperature higher than that of the skin at the point touched feels warm or hot to the touch, while a substance at a temperature lower than that of the skin feels cold to the touch. The sensation is due to the transfer of heat from the substance to the skin in the first case, and from the skin to the substance in the second case. The intensity of the sensation depends upon the quantity of heat transferred, and is, therefore, greatly influenced by the conducting power of the substance touched. Thus, in a room at the ordinary temperature where all the objects are at the same temperature—a little below that of the skin of the hand—bodies of good conducting material, such as metal or (in a less degree) marble, feel quite cold to the touch; while bodies of badly conducting material, such as wood or cloth, give only a very slight sensation of coldness, and, therefore, appear to be much warmer than the other objects touched, although they are at exactly the same temperature. Similarly, when a body hotter than the skin is touched, the intensity of the sensation experienced depends very largely on the conducting power of the substance touched. Thus, a very hot piece of wood may be touched with impunity, but a piece of metal at the same temperature would inflict a serious burn.

> It must be remembered that the temperature sensation experienced on touching any substance depends upon the temperature of the skin at the point touched. For example, if the right hand is immersed in hot water and the left in cold water for some minutes and both hands be then plunged into lukewarm water, the right hand will, at first, experience a sensation of cold and the left hand a sensation of warmth. Ultimately, however, the sensation will be the same in both hands, and this will be one of warmth or cold according as the temperature of the water is above or below the normal temperature of the human body.

3. **Effects of Heat.**—When a substance is heated or cooled certain characteristic effects are produced. The nature of the effects produced in any particular case depends upon the sub-

stance dealt with, and upon the conditions under which the heating or cooling takes place ; the most important effects are, however, included under the following four heads :—

I. **Change of Temperature.**—The substance may become hotter or colder.

II. **Change of Volume.**—The substance may expand or contract.

III. **Change of Physical Properties.**—The elasticity, the viscosity, the specific heat, the conductivity, the refractive index, and other physical constants of the substance may change in value.

IV. **Change of Physical State.**—The substance may change from one of the three states of aggregation as a solid, a liquid, or a gas, into another.

These changes do not all take place under the same conditions, but each change is, under certain conditions, a true effect of heating or cooling the substance. The first three effects, I., II., and III., are generally produced at the same time, when the substance heated or cooled does not undergo a change of state. These four effects are also reversible, in the sense that whatever change may be produced when the substance is heated is exactly reversed when the substance is cooled to its original state. In other words, when the heat change causing the effect is reversed the effect itself is reversed. Thus, if the substance expands when heated, it contracts when allowed to cool ; if it melts when heated, it solidifies when it cools ; if it vaporises when heated, it condenses when it cools.

There are other effects incidental to the heating or cooling of a substance which cannot be considered as general and regular effects of this cause. Thus some substances when heated or cooled undergo certain molecular changes which greatly alter their physical properties. For example, steel and other metals may be hardened or softened by heating or cooling ; iron and

some other metals become soft and capable of welding when sufficiently heated; in the same way glass, sealing wax, and other similar substances pass through a plastic stage when heated to the melting point.

Experience shows, too, that chemical action is in many cases the direct effect of heating a substance. Thus many compound substances undergo chemical decomposition when heated, and other substances when heated together enter into active chemical combination. Potassium chlorate, for example, is decomposed when heated into potassium chloride and oxygen; calcium carbonate or limestone, when heated, is decomposed into quick-lime and carbon dioxide; and coal, when heated in retorts, undergoes destructive distillation and produces coke, coal gas, ammonia, and other products.

A piece of coal exposed to the air under ordinary conditions does not combine with the oxygen of the air at ordinary temperatures, but if the coal is heated to a sufficiently high temperature the carbon and hydrogen of the coal combine with the oxygen, and the process of combustion thus started is maintained until the coal is all consumed. The chemical effects of heat are really instances of the transformation of heat into chemical energy or of chemical energy into heat, and are best considered from that standpoint.

4. **Change of Temperature.** — It has already been explained that, when a substance is heated, or gains heat, its temperature rises, and when it is cooled, or loses heat, its temperature falls. This statement is merely a repetition of the explanation already given of the meaning of temperature, but it must be noted that it is generally true only when the substance heated or cooled remains throughout the process in the same state of aggregation as a solid, a liquid, or a gas. It will be found later that when a substance changes state it may, *during the change*, gain heat without showing a rise of temperature, or lose heat without showing a fall of temperature. Thus, melting

ice absorbs heat in melting without rising in temperature, and boiling water absorbs heat during vaporisation without rise of temperature. Similarly, steam in condensing to water at the same temperature gives out heat, and water in freezing to ice at the same temperature also gives out heat; in both cases the substance loses heat, but there is no fall in temperature. When, however, a substance which remains throughout the process in the same physical state gains heat its temperature rises, and when it loses heat its temperature falls. Similarly, when the temperature of a substance in a given physical state rises, it may be inferred that it is gaining heat, and when the temperature falls it may be inferred that it is losing heat.

5. **Change of Volume.**—In order to find out how the volume of a substance is affected when the substance is heated or cooled, it is necessary to resort to experiment.

Experiment 1.—Get a flat strip of iron about 2 feet long, and set it up as shown in Fig. 1. One end rests on a block and abuts on the

Fig. 1.

side of a ledge screwed to the top of the block. The other end rests on a roller made of a short length of a knitting pin placed on the surface of another block at right angles to the length of the strip. A light pointer is attached to one end of the roller at right angles to its length, and is thus able to indicate by its motion on a circular scale any rotation of the roller on which the strip rests. The strip is thus mounted in such a way that if it expands or contracts when heated one end remains fixed, but the other end is free to move by rolling on the pin on which it rests.

Now arrange two or three Bunsen burners or spirit lamps, as shown in the figure, so as to heat the strip strongly along the greater part of its length, and note the result.

It will be found that the motion of the pointer indicates a gradual expansion of the strip as the heating proceeds. Also, if the Bunsens be removed it will be found that as the strip cools to its

original temperature, it also contracts slowly to its original length. The experiment may be repeated, with the same general result, with strips of many different materials.

It will be noticed that in all cases the expansion caused by heating is extremely small. Rough quantitative results may be deduced from the experiments by noting that a complete revolution of the pointer would correspond to an expansion of the strip equal to the circumference of the roller. The sensitiveness of the apparatus for detecting expansion is therefore increased by using a rolling pin of small diameter. The surface of the roller and the surfaces in contact with it should be slightly roughened to prevent slipping.

This experiment indicates that when a solid substance is heated without undergoing change of state its linear dimensions in general increase. That is, the substance, as a general rule, expands, and its volume increases when it is heated, and contracts when it is cooled.

Fig. 2.

Experiment 2.—Take a small flask and fit a length of 6 or 8 inches of small bore tubing (about 1 mm. bore) into it with a rubber stopper, as shown in Fig. 2. Fill the flask with coloured alcohol, and then insert the stopper so as to force the liquid up into the tube. In doing this care must be taken to exclude all air from the flask and tube, and to arrange matters so that the liquid completely fills the flask and tube to a point halfway up the tube.

It will be seen that with this apparatus any change in the volume of the liquid will be indicated by the rise or fall of the liquid in the tube, and that even a very small change of volume can be detected in this way if the bore of the tube is small compared with the capacity of the flask. The alcohol here is coloured merely in order that the column in the tube may be plainly visible.

Now place the flask in a beaker of warm water. It will be found that as the liquid in the flask absorbs heat the level of the liquid in the tube rises rapidly, thus indicating that the liquid expands when heated.

If the flask is now taken out of the warm water, and the liquid allowed to cool to its original temperature, it will be found that it contracts to its original volume as indicated by the height of the

liquid column in the tube. If again the flask is immersed in ice-cold water the liquid will be cooled, and in cooling will be seen to contract. Also, when the flask is removed from the cold water, and the liquid allowed to recover its original temperature, it will be found that it gradually expands until it regains its original volume.

This experiment may be repeated with a number of different liquids with the same general result.
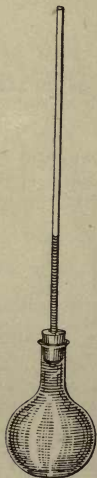
Experiment 3.—Get a small flask and fit a length of 6 or 8 inches of narrow glass tubing (about 3 mm. bore) into it with a rubber stopper, so that the lower end of the tube comes, as shown in Fig. 3, nearly to the bottom of the flask. Care must be taken to make sure that the fitting of the tube into the neck of the flask with the rubber stopper is perfectly airtight.

Place a small quantity of coloured alcohol in the flask, and then fit the tube and stopper in tightly. It will be found when this is done that a short column of alcohol has been forced up into the tube.

It will be seen that by this arrangement a quantity of air is confined in the flask between the surface of the liquid and the cork, and that any change in the volume of this air will be indicated by a corresponding rise or fall of the column of liquid in the tube.

Place the hand on the surface of the flask so as to warm the confined volume of air.

It will be found that, even with this slight heating, the air expands considerably, and may force the liquid to the top of the tube, or even cause it to overflow.

When the hand is removed the air cools, and, as it cools, contracts.

This experiment may be repeated with the same general result, with a number of different gases instead of air.

Fig. 3.

These experiments show that certain solids, liquids, and gases expand when heated, and contract when cooled. If experiments of this type are extended so as to test the behaviour of a very large number of substances in each state, it becomes possible to determine with some certainty whether this result is true generally for all substances. Experimental work of this kind has been carried out, and it is found, as a general rule, that

substances, whether solid, liquid, or gaseous, expand when heated and contract when cooled. This general rule applies, however, only to substances which remain in the same physical state during the process of heating or cooling, and has no reference to the changes of volume which accompany change of state.

There are several exceptions to the rule, and there is, in the case of water, a very notable and important exception. Water, when heated from its freezing point, at first contracts, until a slightly higher temperature is reached, and then expands.

It can be seen from the results of the experiments described above that substances differ greatly in expansibility, and that, as a general rule, a gas is more expansible than a liquid, and a liquid is more expansible than a solid.

6. **Change of State.**—When a substance is heated it may, under certain conditions, undergo change of state from a solid to a liquid, or from a liquid to a vapour or gas without change of temperature. Thus, when ice at its melting point is heated, it changes, under normal conditions, from the solid state as ice into the liquid state as water without rise of temperature during the progress of the change; similarly, when water at its boiling point is heated, it changes, under normal conditions, from the liquid state as water into the gaseous state as steam without rise of temperature during the progress of the change.

In the same way, when a substance is cooled, it may, under certain conditions, undergo change of state from the gaseous state to the liquid state, or from the liquid state to the solid state without change of temperature. Thus, when steam at its condensing point is cooled under normal conditions, it *condenses* or changes from the gaseous state as steam into the liquid state as water without fall of temperature during the progress of the change; also, when water at its freezing point is cooled under normal conditions, it *freezes* or changes from the liquid state as water into the solid state as ice without fall of temperature during the progress of the change.

The phenomena which attend change of state are dealt with in detail later, but it may be noted here that change of state is generally accompanied by a change in volume. This change of volume is, however, quite different in character from that dealt with in the foregoing article. It may be comparatively small, as is generally the case in a change from the solid to the liquid state, or very great, as in the case of a change from the liquid state to the gaseous state, but it is, in all cases, the natural accompaniment of a complete change in the physical state of the substance.

CHAPTER II.

THERMOMETRY.

7. The Principle of the Thermometer.—When a definite mass of any substance is heated without undergoing change of state its temperature rises, and, at the same time, its volume increases. Similarly, when the mass is cooled its temperature falls and its volume decreases. Further, whether the mass is heated or cooled it is found that it always occupies the same volume at the same temperature ; that is, any given volume always indicates the same temperature.

It follows from this that the temperature of a body may be indicated by its volume and that any change of temperature may be detected by the corresponding change in volume. For example, if the small flask and tube filled with coloured alcohol, as described in Experiments 2 and 3, be heated or cooled, its rise or fall of temperature is at once indicated by the rise or fall of the column of liquid in the tube, and the level at which the top of this column stands in the tube may be taken as an indication of the temperature of the alcohol or of the air.

Further, if the flask is immersed in a bath of water it quickly takes the temperature of the water, and the position of the liquid column in the tube, although it primarily indicates the temperature of the alcohol in the flask, indicates also the temperature of the water in the bath.

The flask and tube filled with alcohol may thus be used to compare temperatures. For example, if it is immersed successively in a number of different baths of water, and the level of the liquid in the tube is noted in each case as soon as it becomes steady, it is possible to give at once the relative order

of the baths in point of temperature, and to obtain a general idea of the differences of temperature which exist between them. In the same way if the flask be placed in a suitable position in a room, the changes in the level of the liquid in the tube may be taken to indicate, from hour to hour and from day to day, the changes in the temperature of the room.

The usefulness of this apparatus for purposes of this kind will obviously be increased by using a large bulb and stem, similar to that shown in Fig. 4, instead of the flask and tube, and by graduating the stem in divisions of any convenient length. In this form the instrument may be immersed in any liquid, for the purpose of testing its temperature, without risk of leakage or of injury to a rubber stopper, and the level of the liquid in the stem can at any time be read off on the scale engraved on the stem.

An instrument of this kind can evidently be used within certain limits as a simple form of temperature indicator, but it will be understood that it is of very little general use for the definite specification of temperature. It is useless, for example, to specify the temperature of a bath of water by stating that the alcohol in the stem of the indicator immersed in it stands at a particular division of the scale. No division of the scale has been marked to indicate any known temperature, and the scale itself is quite arbitrary in character, so that the temperature indicated by any division on the scale is quite indeterminate.

Fig. 4.

It is necessary, therefore, in order to adapt the instrument for the purpose of comparing and specifying temperatures to make certain improvements in its construction.
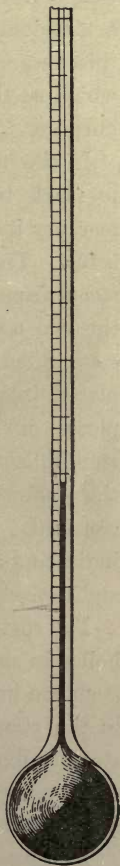
In the first place it is necessary to decide on a suitable liquid with which to fill the bulb and stem. Alcohol is not very suitable for general use, because it boils at a comparatively low temperature, and cannot, therefore, serve as an indicator through a sufficiently wide range. Mercury is much more suitable in this respect, and, as it is specially suitable in other respects which need not here be considered, it is generally used for this purpose.

In the next place it is necessary, before graduating the stem, to mark two points on the stem at which the column of the mercury indicates two well known and naturally fixed temperatures. The temperature of melting ice and the temperature of steam from water boiling at the normal atmospheric pressure are the two temperatures selected for this purpose. The bulb and stem, filled with mercury to a convenient point in the stem, is placed in a large beaker and completely surrounded with small pieces of melting ice. The column of the mercury in the stem falls to a certain point at which it remains steadily fixed, thus showing that the temperature of melting ice is quite constant. This point is marked on the stem as a **fixed point**, indicating a known temperature which can be definitely specified and reproduced if required.

The instrument is then fitted into a large flask or small copper boiler in such a way that the bulb and the greater part of the stem are immersed in steam from boiling water. The mercury in the stem now rises to a certain point at which it remains steadily fixed, thus showing that the temperature of the steam is quite constant. This point is also marked on the stem as a second **fixed point,** indicating a known temperature.

Two fixed points have now been marked on the stem; each point indicates a definitely known temperature, and the difference of temperature corresponding to the rise or fall of the mercury column from the one point to the other is definitely fixed and constant. This difference of temperature, the difference between

the melting point of ice and the boiling point of water, may now be divided into any number of **degrees** or steps by any convenient method. The most obvious method is to divide the volume of the bore of the stem between the two fixed points into a certain number of equal parts, and to graduate the stem between these two points in accordance with this mode of division. If the bore of the stem is uniform, this graduation is easily effected by dividing the distance between the two points into the required number of equal parts. The scale thus obtained between the two fixed points on the stem divides the range of temperature between these two points into a certain number of steps or degrees in a perfectly definite and systematic manner. It is to be noted, however, that the degrees are not necessarily equal; by the method of division the degrees correspond to equal changes* in the volume of the mercury in the instrument, but it cannot be assumed that equal changes in the volume of the mercury indicate equal changes in its temperature.

Notwithstanding this difficulty this is the method generally adopted for deriving a **scale of temperature** from the difference of temperature between the two fixed points selected as the basis of the scale. The scale obtained between the two fixed points on the stem of the bulb can obviously be extended above and below the fixed points, and may, therefore, be used for the specification of any temperature which lies within the range of the instrument.

It must always be remembered, however, that a scale of temperature obtained in this way is not independent of the properties of the liquid used in the bulb. That is, if the scale is derived by exactly the same process for two different liquids the temperature indicated by the divisions of the scale will not be the same in the two cases. This is evidently due to the fact that equal changes in the volume of the liquid do not necessarily correspond to equal changes of temperature, and that the degrees

* See Art. 21.

of temperature determined by this method may, therefore, vary with the liquid used in the bulb.

In order to obtain a standard scale of temperature it is, therefore, necessary to select a standard liquid for use in the bulb. Mercury is generally selected for this purpose, and experience shows that it has the advantage that the degrees of temperature into which it divides the range between the fixed points are practically equal.

It is necessary also to specify the material of the bulb and stem, for the changes in volume which determine the degrees of the scale of temperature evidently depend upon the expansion of the bulb and stem as well as upon the expansion of the liquid. Glass of standard composition and known expansibility is the material generally adopted for this purpose.

Hence, if we construct a bulb and stem of standard glass, fill it with pure mercury, and graduate the stem by the method described above, taking certain precautions, to be described later, we obtain an instrument which can be used for the accurate determination of temperature on a standard scale of temperature which is definitely specified and generally accepted. An instrument intended for this purpose is called a **thermometer,** and the type of thermometer just described is generally known as a **mercury-in-glass thermometer.** A thermometer is thus an instrument used for the determination of temperature, and all matters pertaining to the determination of temperature are included under the term **thermometry**.

8. **Construction of a Mercury-in-Glass Thermometer.** —The form of tube generally used for the construction of a mercury-in-glass thermometer is shown in Fig. 5. As shown in the figure, the bulb is a narrow cylindrical bulb about half an inch long and a tenth of an inch in diameter. The walls of the bulb are very thin, and its external diameter is slightly less than that of the stem to which it is attached. The stem is of thick-walled capillary tubing of very fine bore. The length of the

stem and the diameter of the bore are adjusted to the capacity of the bulb and the range of temperature for which the thermometer is designed. The stem is closed at the upper end, but the bore ends there in a small overflow bulb which allows the mercury to expand without bursting the tube should the instrument be heated beyond the range for which it is intended.

The graduations giving the scale of temperature are etched on the glass of the stem, the finely-etched lines being generally filled in in black or red in order that they may be more easily read.

The processes of filling and graduating a thermometer as carried out by a skilled instrument maker involve too many technicalities to be considered here. The simpler method described in the experiments given below may, however, be carried out in the laboratory.

The following experiment describes a convenient method of filling a thermometer tube :—

Experiment 4.—Obtain a thermometer tube similar to that shown in Fig. 6. Pour some mercury into the open bulb at A, then warm the bulb B very gently by passing it a few times through the flame of a Bunsen burner. The air in the bulb B is thus heated and expands, so that some of it bubble through the mercury at A, and escapes from the tube.

Fig. 5.   Fig. 6.

Now allow the tube to cool ; the air in the tube cools, and as it cools its pressure decreases, and mercury is forced from the bulb A down into the bulb B.

Repeat this process of alternate heating and cooling until the bulb B is nearly full of mercury. Then heat the bulb carefully until the

2

mercury boils gently, and keep it boiling very quietly for about a minute or so, until every trace of air and moisture is expelled from the tube by the mercury vapour. Now let the mercury in the bulb cool very slowly, and it will be seen that as it cools and the vapour condenses, the mercury from the bulb A enters the tube and soon fills it completely.

Now heat the mercury in the tube nearly to its boiling point ; this is best done at this stage by immersing the bulb B in some mercury which is kept at the boiling point in a crucible. While the mercury is at this temperature bring a blowpipe flame to bear on the narrow part of the stem a little below the bulb A, and seal off the tube at this point.

When the tube cools after this operation the mercury contracts, and the thread of mercury in the stem should stand at a point consistent with the range for which the instrument is intended. This will be the case if the length and bore of the stem are properly adapted to the capacity of the bulb.

The tube is now filled ready for graduation, but it should stand for some days before it is graduated. The glass takes some time to recover from the heating to which it has been subjected ; it continues to contract slightly for hours after it has quite cooled, and may take several days to regain its original volume.

The first step in the graduation of the thermometer is the determination of the fixed points of its scale. As stated above, the two fixed points generally adopted are the melting point of ice at the normal atmospheric pressure (760 mm. mercury at the sea level in latitude 45°) and the boiling point of water under the same normal pressure. The melting point of pure ice is very slightly affected by change of pressure, and may be taken as constant at all ordinary atmospheric pressures. The boiling point of water, however, changes appreciably with change of pressure, as will be explained later. It rises as the pressure increases, and falls as the pressure decreases, and it is found that for the small deviations from the normal which usually takes place in the atmospheric pressure, a change of 1 mm. in the pressure causes a change in the boiling point of about $\frac{1}{2700}$ of the normal interval between the melting point of ice and the boiling point of water.

The lower fixed point, the melting point of ice, or, as it is sometimes called, the freezing point of water, may be determined in the following manner :—

Experiment 5.—Place the thermometer tube filled with mercury in a beaker, a large funnel or other suitable vessel, and surround the bulb and the lower part of the stem with small pieces of ice, as shown in Fig. 7. Suitable pieces are readily obtained by chipping them off a
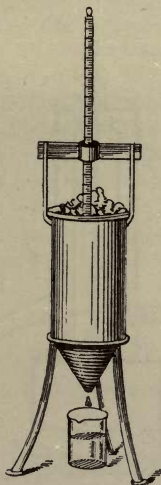
Fig. 7.

block of ice with the point of a knife or a stout needle or bodkin ; before piling them round the thermometer the pieces should be thoroughly washed in clean water.

The thread of mercury in the stem will now be seen to stand steadily at a fixed point indicating the melting point of ice.

Mark this point on the stem by a fine file mark, or better, by means of a fine line drawn by a needle point on a thin strip of wax previously melted on to the stem for this purpose.

This mark gives the lower fixed point of the scale, and indicates the melting point of ice or the freezing point of water. It is very commonly called the **freezing point.**

The upper fixed point, the temperature of water boiling under the normal atmospheric pressure, may be determined in the manner described below.

Experiment 6.—Obtain a steam heater of the form indicated in Fig. 8. Half fill the bottom part of the heater with water, and fit the thermometer tube through a cork in the opening in the lid of the heater. The bulb and a good part of the stem should be
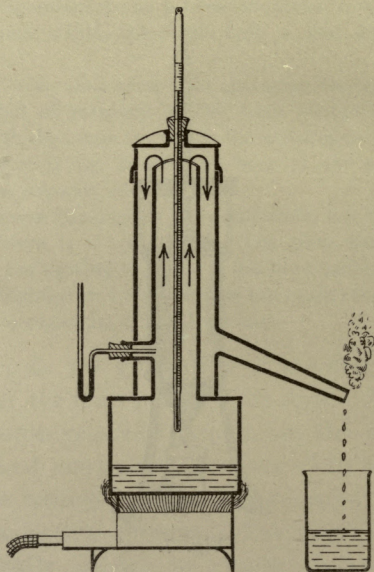
Fig. 8.

inside the heater, but the bulb should be quite clear of the water at the bottom. Place the heater on a suitable burner, and let the water boil vigorously. The steam from the boiling water rises up the central tube in the upper part of the heater, and then passes downwards between this tube and the outer wall to the side tube as shown in the figure.

The thermometer in the central tube is thus surrounded by steam, which is protected from the cooling effect of the outer air by the *jacket* of steam in the space surrounding it. The steam is thus maintained throughout the central space at the temperature at

which it is produced, and the thermometer tube immersed in this steam is thereby subjected to the temperature of steam from water boiling at the existing atmospheric pressure.

Adjust the position of the thermometer tube in the cork until the top of the mercury column in the stem is just visible above the cork. When the level of the column is quite stationary mark the point at which it stands by a fine line on the stem as in the case of the lower fixed point. This mark really indicates the boiling point of water under the existing atmospheric pressure, and ought, in strict accuracy, to be corrected for any difference between that pressure and the normal pressure. This correction is, however, extremely small, and can be made negligibly small by making this determination on a day when the height of the barometer is very nearly equal to the normal height of 760 mm.

The correction may, however, be made with sufficient accuracy in the following manner. As soon as the point indicating the boiling point of the water is marked, read the barometer, and reduce the observed height to the equivalent height at 0° C. Let the difference between this height and 760 mm. be h mm. Then measure the distance between the two points marked on the stem of the thermometer, and let this distance be denoted by l in any convenient units. Then, from the result quoted above, it can be seen that the necessary correction may be made approximately by raising or lowering the boiling point mark on the stem through a distance $\dfrac{hl}{2700}$, according as the reduced height of the barometer at the time of the experiment is less or greater than 760 mm. Thus, if the reduced barometric height were 750 mm., and the distance between the marks made on the stem 135 mm., the mark indicating the boiling point under the existing pressure should be raised about half a millimetre to indicate the boiling point at the normal pressure. In this way the upper fixed point, generally known as **the boiling point**, is marked on the stem of the thermometer.

When the fixed points are marked on the stem the thermometer is ready for graduation. Two scales of graduation are in common use at the present time.

On the **Centigrade scale,** due to Celsius of Upsala, the freezing point is marked as the zero of the scale, and the bore between the freezing point and the boiling point is divided into 100 equal parts. The boiling point on this scale is thus marked

100°, and the range of temperature between the freezing point, 0°, and the boiling point, 100°, is divided into 100 **degrees**. These degrees are not, as already explained, **necessarily** equal; any particular degree on the scale is merely the change of temperature which corresponds to the expansion of the mercury from one particular division of the scale to the next, and any particular temperature on the scale is the temperature indicated when the mercury stands at a particular division of the scale.

Temperatures on this scale are written as °C., such as 10° C., 20° C., 90° C. The scale, when constructed between the fixed points, may be extended above and below these points. Thus we may have 105° C., 110° C., 120° C., 200° C., &c., above the boiling point, and − 5° C., − 10° C., − 20° C., &c., below the freezing point. The Centigrade scale is the one in common use on the Continent, and is generally used everywhere in scientific work.

On the **Fahrenheit scale,** introduced by Fahrenheit of Dantzic about 1714, the freezing point is marked 32°, and the bore of the stem between the freezing point and the boiling point is divided into 180 equal parts. The boiling point on this scale is thus marked 212°, and the range of temperature between the freezing point, 32°, and the boiling point, 212°, is divided into 180 **degrees**. As before stated, these degrees are not necessarily equal; any particular degree on the scale is merely the change of temperature which corresponds to the expansion of the mercury from one particular division of the scale to the next, and any particular temperature on the scale is the temperature indicated when the mercury stands at a particular division of the scale.

The zero of this scale is 32° below the freezing point, and is marked 0°; it indicates the lowest temperature known in Fahrenheit's time, the temperature of a mixture of ice and snow.

Temperatures on this scale are written as °F., such as 10° F., 100° F., 200° F.; and the scale is extended above and below

the fixed points, so that we have temperatures such as 300° F., 400° F., &c., above the boiling point, and 20° F., 10° F., 0° F., − 10° F., − 20° F., &c., below the freezing point.

The Fahrenheit scale is the scale in common use in England for all purposes except those of Science.

The relation between these two scales is shown clearly in Fig. 9, which shows two thermometers, a **Centigrade** thermometer, graduated on the Centigrade scale, and a **Fahrenheit** thermometer, graduated on the Fahrenheit scale. Since the **same range** of temperature, that between the freezing point and the boiling point, is divided into 100° on the Centigrade scale and into 180° on the Fahrenheit scale, it follows that any range of 5 Centigrade degrees is represented by a corresponding range of 9 Fahrenheit degrees. Hence, if C and F denote the same temperature on the Centigrade and Fahrenheit scales respectively—

$$\frac{C}{F-32} = \frac{100}{180} = \frac{5}{9}.$$

That is,

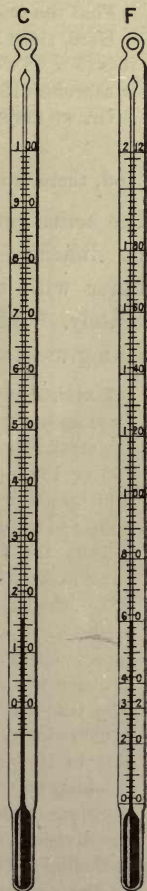$$C = \frac{5}{9}\ (F-32),$$

or,

$$F = \frac{9}{5}\ C + 32.$$

Fig. 9.

Numerical Examples.—Find the reading on the Fahrenheit scale corresponding to 15° C.

Here, since 15° C. is 15 Centigrade degrees above the freezing point it is ($\frac{9}{5} \times 15$), or 27 Fahrenheit degrees above the freezing point, and is therefore represented on the Fahrenheit scale as 59° F.

Or, we may write :

$$F = \tfrac{9}{5} \times 15 + 32 = 59,$$

and, therefore, 59° F. is the same temperature as 15° C.

Find the reading on the Centigrade scale corresponding to 50° F.

Here, since 50° F. is 18 Fahrenheit degrees above the freezing point it is ($\tfrac{5}{9} \times 18$), or 10 Centigrade degrees above the freezing point, and is therefore 10° C. on the Centigrade scale.

Or, we may write :

$$C = \tfrac{5}{9} (50 - 32) = \tfrac{5}{9} \times 18 = 10,$$

and, therefore, 10° C. is the same temperature as 50° F.

The actual process of graduating a thermometer is a matter of great difficulty and requires special methods and apparatus, together with the skill of the expert worker, to carry it out accurately. The process may, however, be attempted by the following method in the laboratory.

Experiment 7.—Measure carefully the distance between the two fixed points on the stem of the thermometer tube and construct, along the straight edge of a sheet of paper, a scale dividing this length into 100 or 180 equal parts, according as the graduation is to be on the Centigrade or Fahrenheit scale. Extend this scale beyond the fixed points so as to correspond to the length of the tube to be graduated.

Take the thermometer tube and coat it with a thin coating of paraffin wax by immersing it for some seconds in hot melted wax. When the tube cools after immersion it will be covered with a thin transparent coating of wax. Now rule with a fine needle point four lines lengthways on the tube in the manner indicated in Fig. 10, and transfer the scale from the paper edge to one of the outside lines. The transfer is conveniently effected by fixing the paper strip with rubber rings on the tube so that the scale lies accurately along the line in its proper position relative to the fixed points, and then pricking off with a needle point the points on the line opposite the divisions of the scale. When the scale is fully marked off in this way the divisions on the stem should be ruled and numbered in the manner indicated in the figure. The lines should be ruled through the wax to the glass with a fine needle point. They can be ruled easily and quickly with the aid of a short length of glass tubing with straight ends, which fits loosely over the thermometer tube ; one end of the tube is used as a ruler as it is moved along from division to division on the scale. When the scale is completely ruled and numbered, the tube should be exposed to the action of hydrofluoric acid gas, obtained

by the action of strong sulphuric acid on fluor spar in a lead trough. The action of the gas etches the glass along the lines exposed by the needle point and quickly gives a clearly marked scale of sharp even lines.

It will be noticed that the method of graduation adopted in this experiment assumes that the bore of the thermometer tube is quite uniform, for the distance between the fixed points is divided into equal *length divisions* in order to divide the capacity of the bore of the tube between these points into a corresponding number of equal *volume divisions*. If the tube is a good one the bore will be fairly uniform, and the errors of the scale due to want of uniformity in this respect will be negligibly small. The bore is, however, easily tested by noting the length which a short thread of mercury occupies at different points in the tube. Should the bore prove to be irregular it may be necessary to determine the correction to be applied at any point in the scale ; this correction is evidently proportional to the deviation of the cross-section of the bore at that point from its average value, and can therefore be derived from a tabular statement or curve showing the length occupied by the short thread of mercury at different points in the tube. This process of correcting a thermometer scale for variation in the bore of the stem is known as the *calibration* of the stem ; it is an exceedingly difficult and troublesome process, and cannot here be considered in detail.

Fig. 10.   Fig. 11.

The usual form of the finished mercury-in-glass thermometer intended for accurate scientific work is shown in Fig. 9. Cheaper forms of the instrument are generally constructed with a small spherical bulb and mounted on a wood or metal frame, on which the scale is engraved. A good form of cheap thermometer for ordinary use is the German bath thermometer shown in Fig. 11 ; in this form the scale is
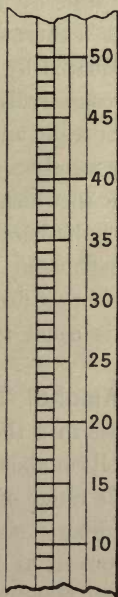
engraved on a strip of porcelain or paper attached to the thermometer tube and protected by a wide glass tube which surrounds the stem and is hermetically sealed to it.

Mercury boils at 357° C. and freezes at − 39° C., so that the range of temperature within which a mercury-in-glass thermometer can be used lies between these temperatures. A thermometer intended to indicate temperatures within a range which does not include the fixed points is graduated by fixing two convenient points on its scale by means of another thermometer of suitable range. Thus a thermometer ranging from 200° C. to 300° C. could be graduated by determining the points on its stem which correspond respectively to these two temperatures as the " fixed points " of its scale, and then dividing the stem between the two points in the usual way.

The extent to which the scale of a thermometer is subdivided depends upon the bore of the capillary tube and the purpose for which the instrument is intended. For ordinary purposes the scale usually shows degrees or half-degrees. For more accurate purposes it is usual to divide the degree divisions into fifths or tenths.

9. **The Alcohol Thermometer.**—Alcohol is not suitable for general use in a thermometer on account of its low boiling point. It boils at about 79° C., and cannot, therefore, be used for a considerable range of temperature which comes well within the limits of ordinary observation and experiment. Its freezing point is, however, as low as − 94° C., or nearly 60° C. lower than that of mercury, so that it is specially suitable for thermometers intended for use at very low temperatures.

In addition to this special characteristic alcohol is, within the range of temperature for which it is available, well suited in many ways for use in a thermometer. It is highly expansible with rise of temperature, so that a thermometer containing it is very sensitive to change of temperature. It is light, and can, therefore, be used in a tube with a large bulb without unduly

straining the bulb by its weight; it is also a liquid which wets glass, and can, therefore, move easily and smoothly in a tube of very fine bore without any of the difficulties caused by capillarity in the case of mercury. Both these properties are of great value in the construction of a sensitive thermometer, for it is evident that for a given liquid the sensitiveness of a thermometer depends upon the ratio of the capacity of the bulb to the capacity of the bore of the stem per unit length. Alcohol is also cheap, in the form generally used, and it is easily manipulated in the construction of the thermometer. Coloured alcohol is, therefore, very commonly used in the construction of cheap thermometers intended to record ordinary indoor and outdoor temperatures.

Other organic liquids, such as ether and chloroform, have much the same advantages as alcohol for thermometric purposes, but all volatile liquids of low boiling point have the common disadvantage that they vaporise in the thermometer tube and condense in the upper part of the stem. This defect is most troublesome at temperatures near the boiling point of the liquid, but it has always to be borne in mind as a possible source of error. When liquid is found condensed in the upper part of the stem, it can always be displaced by slightly warming the stem or by swinging the tube in the usual way.

All alcohol thermometers are graduated by direct comparison with a mercury-in-glass thermometer, so as to indicate temperatures on the mercury-in-glass scale.

10. **Maximum and Minimum Thermometers.**—A thermometer is sometimes required to record the highest or the lowest temperature which it has indicated during a given period of time. For example, a thermometer may be required to record the highest temperature experienced during the day or the lowest temperature experienced during the night.

A thermometer constructed to record the *highest* temperature experienced during any given period is called a **maximum ther-**

mometer, and a thermometer constructed to record the *lowest* temperature experienced in a given period is called a **minimum thermometer.**

Six's combined maximum and minimum thermometer, shown in Fig. 12, is the oldest thermometer of this type. It is much

Fig. 12.

used by gardeners for horticultural purposes. The bulb A and the stem from A to B are filled with alcohol and constitute the thermometer tube of the instrument. The column of mercury, B C, in the U-shaped bend of the stem, serves merely as an indicator; the movement of the column indicates the expansion or contraction of the alcohol in AB, and the end B indicates temperature on the left-hand scale in the figure, while the end

C indicates the same temperature on the right-hand scale. Two small steel indices, b and c, are placed in the bore of the stem at each end of this mercury column; each index is so constructed, as shown in the small side figure, that while it is easily pushed up the tube in front of the column it is held at any point to which it may be displaced by means of the small side spring shown at s in the figure. The index b, at the end B, is moved upwards in the tube as the temperature *falls*, and the point at which it remains fixed evidently indicates the *minimum* temperature experienced since the index was last set at the end of the column. The index c, at the end C, is moved up as the temperature *rises*, and the point at which it remains fixed indicates, therefore, the *maximum* temperature experienced since the index was last set. In each case the temperature recorded is evidently
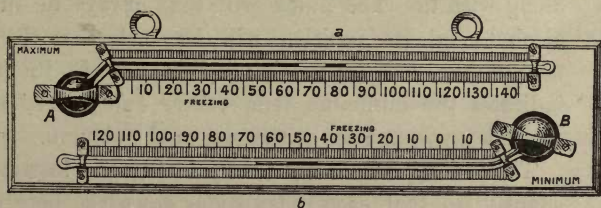
Fig. 13.

that indicated by the lower end of the index. The indices can be set at any time by means of a magnet acting through the glass of the stem.

The portion CD of the stem and the bulb at D are partially filled with alcohol in order to protect the index at C and the mercury from the air and to keep the bore of the stem above C open and free from dust.

Rutherford's maximum and minimum thermometer, shown in Fig. 13, is another instrument in common use. It consists of two separate thermometers mounted horizontally on a wood or metal frame. One thermometer, A, is an ordinary mercury thermometer provided with an index to register the *maximum*

temperature experienced. The index, shown at a, is a light
piece of steel, shaped something like a small dumb-bell, which
the mercury column pushes in front of it as the temperature
rises. As the stem is horizontal, the index remains at the
furthest point to which it is displaced, and the end nearest the
mercury column, therefore, indicates the maximum temperature
experienced since the index was last set at the end of the column.
The other thermometer, B, is an alcohol thermometer provided
with an index in the stem to indicate the *minimum* temperature
experienced. The index, shown at b, is a small piece
of glass or enamel placed in the stem; the alcohol in
expanding readily flows past it without pushing it on
or displacing it, but, in contracting, the surface film
at the end of the liquid column draws the index back
along with it. The index will thus always lie in the
alcohol, and its position will be such that the end
nearest the end of the alcohol column in the stem
indicates the minimum temperature experienced since
the index was last set at the end of the column.
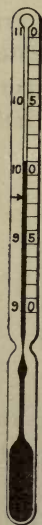
The indices are readily set by tilting the instrument
slightly, so that each index slides down the bore until
it comes to rest with one end in contact with the end
of the liquid column in the tube.

In some forms of maximum thermometers the bore
of the stem, at a point low in the scale is contracted
to very small dimensions. The mercury in expanding

Fig. 14.

easily forces its way past this point, but in contracting
the column breaks at the constriction and the upper
end left in the stem indicates the maximum temperature
reached.

The **clinical thermometer** shown in Fig. 14 is a maximum
thermometer constructed on this plan. The thermometer is used
for taking the temperature of the body. It is usually graduated
on the Fahrenheit scale, and its scale generally extends a few

degrees above and below 98·4° F., which is the normal temperature of the body in health.

The temperature of the body is taken by placing this thermometer in the mouth, or in the armpit or groin, for a short time until it takes the temperature of its surroundings. It is then removed and read; the maximum temperature recorded by it evidently gives the temperature required.

This thermometer and others of the same type are set by swinging them vigorously, bulb downwards, until the mercury in the stem joins with the mercury in the bulb and stem below the constriction.

In **Phillips' maximum thermometer** the bore of the stem is very fine, and the thread of mercury is broken by a small air bubble at a point low in the scale. The portion of the thread above the bubble thus serves as an index for recording the maximum temperature reached. It is pushed on as the temperature rises, but it is left behind by the rest of the mercury in the bulb and stem, as the temperature falls; its upper end therefore indicates the maximum temperature reached.

This thermometer is set, like the clinical thermometer, by swinging the index part of the thread down into contact with the rest of the mercury in the bulb.

11. **Errors of a Mercury-in-Glass Thermometer.**— The mercury-in-glass thermometer is subject to certain errors, of which the following are the most important:—

I. *Change of Zero.*—The tube of a thermometer takes a long time to recover from the heating to which it is subjected in making it and filling it with mercury. It continues to contract appreciably for weeks after the heating is over, and although the greater part of the contraction takes place in the first few weeks, it may be subject to gradual contraction for years.

For this reason most thermometers are subject to a zero error caused by the contraction of the bulb after the fixed

points were marked. As a result of this decrease in the capacity of the bulb, the true zero point is a little higher on the stem than the zero of the scale—that is, the true temperature at any point on the scale is a little lower than that indicated by the actual scale reading. This error is easily corrected by determining at any time the value of the error at the freezing point.

> **Experiment 8.**—Take a thermometer which has been in use for some time and surround the bulb and lower part of the stem with ice as in Exp. 5.
>
> Note the reading of the thermometer when the mercury is steady at 0° C.
>
> It will generally be found that the reading is slightly higher than 0° C. Suppose it to be 0·3° C. Then *the error* at this point on the scale is − 0·3°; that is, 0·3° must be subtracted from the reading at this point to get the correct reading.

II. *Effect of recent Heating.*—This is a temporary error similar in character to the one just considered. A thermometer always takes some hours to recover its original volume after any unusual heating. For this reason if a thermometer is used too soon after recent heating its readings will be too low, for the capacity of the bulb being slightly greater than its normal value the mercury in the stem will, at any given temperature, stand lower than the scale division which indicates that temperature.

III. *Influence of the Temperature of the Stem.*—It is not generally possible to expose the whole of the mercury in the bulb and stem to the temperature to be determined. The mercury in the bulb and lower part of the stem must take this temperature, but the thread of mercury in the stem is frequently at a higher or lower temperature. This evidently causes a slight error in the reading of the thermometer. The correction for this error can be found by calculating the change in the reading which would take place if the mercury in the stem were to acquire the same temperature as that in bulb. It will be shown later that if T denotes the observed temperature, and t the mean

temperature of the mercury in the stem, the corrected temperature is T', is given approximately by

$$T' = T + \cdot 00015 \, n \, (T - t),$$

where n denotes the number of degree divisions of the mercury at the temperature $t°$ C. in the stem.

IV. *Boiling Point Error.*—The correction for the influence of the atmospheric pressure on the boiling point should be made at the time of marking this fixed point.

In testing a thermometer, however, it is generally desirable to test the accuracy of the reading at this point. This can be done as follows.

Experiment 9.—Fit the thermometer into a steam heater as explained in Exp. 6, and note the reading given by the thermometer. Care should be taken to have the bulb and, as far as possible, the whole length of the stem immersed in the steam. Let the observed reading be 99·9° C.

Now read the barometer and calculate the reduced height at 0° C.

Let this reduced height be 751 mm. Now a deviation of 1 mm. from the normal pressure of 760 mm. corresponds approximately, to a change of 0·037° C. in the boiling point. Hence, in this case the boiling point is 0·333° below 100° C. That is, the temperature indicated by the thermometer should be about 99·67° C.

In this example, therefore, the error of the thermometer at the reading 99·9° is − 0·23° C.

When the errors at the boiling point and freezing point are determined by direct observation in this way (Expts. 8, 9), the error at any point on the thermometer scale may be found (if we assume the bore of the tube to be uniform) by setting off the divisions of the scale as abscissæ along an axis, and the errors at the two observed points as ordinates; then if a straight line be drawn, passing through the extremities of these two ordinates, the ordinate of any point on this line gives the error at the scale reading indicated by the corresponding abscissa.

All errors of the thermometer scale arising out of irregularities in the bore can be corrected only by calibrating the bore

3

of the stem. The correction to be applied at any point can be determined with good accuracy from the results of a careful calibration of the stem.

Small changes in the capacity of the bulb, caused by changes in pressure inside or outside the bulb, is another possible source of error in a thermometer. These changes are, however, under ordinary conditions, practically negligible.

CHAPTER III.

EXPANSION OF SOLIDS.

12. **Expansion of Solids.**—It has already been explained that, as a general rule, all solids expand on heating and contract on cooling.

It will now be of interest to find out whether all solids expand equally under the same conditions, or whether different substances differ in their degrees of expansibility. This point can readily be decided by experiments of the type described below.

> **Experiment 10.**—Get a number of flat strips of different metals and other materials, about 2 feet long and half an inch wide, and determine their relative order of expansibility in the following way:—
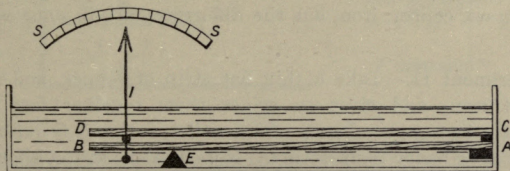
Fig. 15.

Take any two of the strips and set them up inside a long rectangular iron or zinc trough in the manner shown at AB and CD in Fig. 15.

The strip AB rests on a ledge in the trough at A and on a blunt and smooth knife edge at E. The rod CD is placed immediately over AB, resting on a short strip of metal at C, and on a knitting-pin roller at D. The roller carries a light wire index, I, which is counter-poised so that its indications on the scale S may be reliable.

Fill the trough with cold water and allow the apparatus to attain a uniform temperature throughout. Note the position of the index I on the scale.

Now heat the water in the trough gradually, either by blowing steam into it or by means of burners placed below it.

As the temperature rises both strips will expand, but *if one expands more than the other the roller pin between them will turn*, and the index I will move on the scale. If, for example, the upper strip, CD, expands more than the lower, AB, the index will evidently, as the apparatus is arranged in the figure, move to the left.

The motion of the index thus indicates which is the more expansible of the two strips. Both strips are heated under exactly the same conditions through the same range of temperature, and any difference in their expansions must be due, therefore, to a difference in the expansibility of the materials of which they are made.

Compare the strips in pairs in this way, and so determine qualitatively the order of expansibility in which the materials stand.

It will be found that metals, as a rule, are more expansible than other solid substances, such as glass, marble, slate, wood. The order

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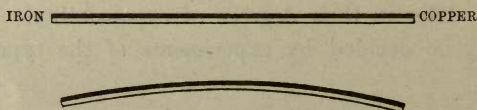
Fig. 16.

of expansibility of the common metals is roughly lead, tin, aluminium, silver, brass, copper, iron, but the differences are in some cases very small.

Experiment 11.—Take a thin flat strip of copper, and a similar strip of iron, and rivet or solder them together face to face. Straighen the compound strip with a mallet, so that it is quite straight and flat at ordinary temperature. Now heat the strip uniformly on a plate of sheet metal with a Bunsen flame, and note the result.

It will be found that the strip takes a curved form as shown in Fig. 16, with the iron on the concave side and the copper on the convex side. This indicates that as the temperature rises the iron expands less than the copper, and the strip is forced to take a curved form with the iron on the inner and shorter side, and the copper on the outer and longer side.

Experiment 12.—Fuse a piece of platinum wire into a glass tube in the usual way.

Now try to fuse a piece of copper or brass wire into a glass tube in the same way, and note the result.

The platinum wire can be fused into glass because platinum and

glass differ very little in expansibility.   Most other metals differ
from glass so much in expansibility that if fused into it, the glass is
cracked by the greater contraction of the metal in cooling.

Another point of interest which presents itself is the relation
between expansion and rise of temperature in solids.   The
degrees of temperature of a mercury-in-glass thermometer
correspond approximately with equal increments in the volume
of the mercury in the tube; this is the basis of the mercury-in-
glass scale of temperature.   It is, therefore, of interest to deter-
mine whether a solid body in expanding expands by equal amounts
for each degree rise of temperature.   This question can be studied
in the case of linear expansion by the following method.

Experiment 13.—Set up the apparatus of **Exp. 10**, as shown in
Fig. 15, with the following modifications :—
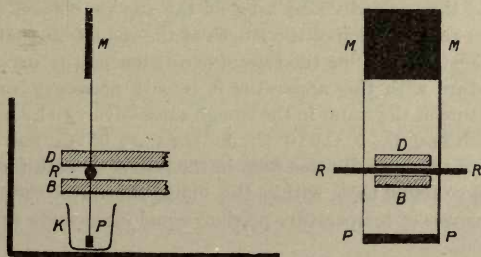
Fig. 17.

The rods AB and CD must be fairly heavy so as to give stability to
the indicator attached to the pin roller as described below.
    The rod AB is to be composed of the alloy invar, an alloy of nickel
and steel which is found to possess such small expansibility that the
change in the length of the rod in this experiment will be practically
negligible.
    The rod CD may be of brass, or copper, or any other material whose
rate of expansion with rise of temperature is to be tested.
    The pointer and scale indicator of Fig. 15 will not be sufficiently
sensitive for this experiment; it must be replaced by the mirror and
scale arrangement shown in Fig. 17.
    The pointer attached to the roller between the rods is replaced
by a light framework carrying a light plane mirror at M, and a strip

of brass at P, as a counterpoise. The construction and arrangement of this indicator are shown clearly in the side and end views given in Fig. 17. In the end view RR represents the roller between the rods which are shown in cross-section at B and D ; MM shows the mirror and PP the counterpoise carried by the frame attached to the roller. The counterpoise P should be protected from currents in the water by a beaker placed as shown at K in the figure.

It will be seen that with this arrangement any expansion of the rod CD will cause the roller R to rotate through a small angle. This will cause the mirror M also to rotate through the same angle. Hence, if an observer directs a telescope towards the mirror M, and focusses it on the image of a vertical scale seen in the mirror, the division of the scale seen at the cross wire in the field of view will change as the rod CD expands and the mirror M rotates. It follows, too, from the arrangement of the apparatus that the change in the reading on the image of the scale is directly proportional to the expansion of the rod.

A telescope is not essential to this arrangement ; an observer looking from any *fixed* point of view at the image of the scale can take the scale division seen at the top or bottom edge of the mirror as an indication of the length of the rod CD at that instant.

In order to determine the rate of expansion of the bar with rise of temperature with this apparatus it is only necessary to adjust the temperature of the water in the trough successively to known temperatures such as 0° C., 5° C., 10° C., 15° C., . . . 95° C., and to take the reading of the scale division seen in the mirror at each temperature.

It will be found that, within the limits of error of the experiment, equal changes of temperature produce equal increments in the length of the rod.

It should be noticed that the simple arrangement of Fig. 15 cannot be used in this Experiment on account of the expansion of the bottom of the trough on which the blocks supporting the rod would rest.

This experiment shows that the expansion of a solid is, in general, directly proportional to the rise of temperature as indicated by a mercury-in-glass thermometer. It must be remembered, however, that this merely means that the law of expansion of a solid is the same as that of mercury.

It follows from this result that if a denote the increase in length, or *linear expansion* of a rod when heated from 0° C. to $t°$ C., the average expansion of the rod *per degree* change of temperature between 0° C. and $t°$ C., is given by a/t. Simi-

larly, if a denote the expansion of the rod when heated from $t'°$ C. to $t°$ C., then $\dfrac{a}{(t - t')}$ gives the average expansion *per degree* between the temperature $t'°$ C. and $t°$ C.

13. **Linear and Cubical Expansion.**—When a body is heated and expands its linear dimensions increase, the areas of its faces increase, and its volume increases. Increase in any linear dimension—that is, increase in length—is usually called **linear expansion**; increase in area is called surface expansion, or **superficial expansion**; and increase in volume is called volume expansion or **cubical expansion.**

If the substance is isotropic—that is, if its properties are the same in all directions at any point in it—it expands equally in all directions, and there will, therefore, be a simple relation between its linear, superficial, and cubical expansions. Hence, in studying the expansion of a solid experimentally, it is necessary to determine only one of these expansions. The linear expansion may be determined by measuring the change in the length of any convenient dimension of the body, or the cubical expansion may be determined by measuring the change in the volume of the body. The superficial expansion is seldom considered, for it could be determined only by making length measurements as in the determination of linear expansion.

It will be understood that while a solid exhibits linear, superficial, and cubical expansion, a fluid—that is, a liquid or gas—can exhibit only cubical expansion. The form and dimensions of the space which a quantity of any fluid occupies are determined by the vessel which contains it, and the change in the dimensions of this space when the fluid is heated, depends upon the expansion of the vessel, as well as upon the expansion of the fluid. A fluid cannot, therefore, be said to exhibit linear or superficial expansion. The volume of the fluid is, however, perfectly definite, and its cubical expansion is indicated by the change in volume which it undergoes on heating.

14. Coefficients of Expansion.—The linear expansion of any body along any line in it may be determined by measuring the change in the distance between any two points on the line. Thus, the linear expansion of a rod in the direction of its length, when heated through any given range of temperature, is determined by measuring the increase which takes place in its length or in any portion of its length.

The actual change of length observed obviously depends on the initial length in which the change takes place, and also upon the change of temperature to which the body is subjected. If, however, we calculate from the data of the experiment the expansion per degree change of temperature for each unit of the initial length we get a constant, which depends only upon the material of the rod. This constant is known as the *coefficient of linear expansion* of the material.

The coefficient of linear expansion of any solid may, therefore, be defined as the ratio of the linear expansion per degree Centigrade to the initial length at 0° C. It will be noticed that the coefficient is here defined in relation to the degree Centigrade, and that the initial length involved in the ratio is the initial length at 0° C.

It is of course permissible to frame a similar definition in relation to the degree Fahrenheit or to take the initial length at any specified temperature, but the definition here given is the one usually adopted.

Hence, if a denote the linear expansion of a length, L, in any solid when heated uniformly from 0° C. to t° C., the coefficient of linear expansion of the solid, as defined above, is given by

$$l = \frac{a}{Lt}.$$

This coefficient is really the *mean* coefficient of linear expansion between 0° C. and t° C., for a/t is the mean or average expansion per degree between 0° C. and t° C.

Similarly, if l denote the mean coefficient of linear expansion of the solid between $0°$ C. and $t°$ C., then any unit of length at $0°$ C. becomes $(1 + lt)$ units of length at $t°$ C., and L units of length at $0°$ C. therefore becomes L $(1 + lt)$ units at $t°$ C. That is, if L_o denote any length at $0°$ C. and L_t the corresponding length at $t°$ C., we have

$$L_t = L_o (1 + lt),$$

where l denotes the mean coefficient of linear expansion of the material of the body between $0°$ C. and $t°$ C.

Similarly, the cubical expansion of a substance may be determined by measuring the increase in volume which a known volume of it undergoes when heated through a known change of temperature, and the **coefficient of cubical expansion** may be defined as the ratio of the cubical expansion per degree Centigrade to the initial volume at $0°$ C.

It follows, as in the case of linear expansion, that if v denote the increase in volume of a volume, V, of any substance when heated uniformly from $0°$ C. to $t°$ C., the mean coefficient of cubical expansion of the substance between $0°$ C. and $t°$ C. is given by

$$c = \frac{v}{Vt}.$$

Also, if V_o denote the volume of the substance at $0°$ C., and V_t the volume at $t°$ C. we have

$$V_t = V_o (1 + ct),$$

where c denotes the mean coefficient of cubical expansion of the substance between $0°$ C. and $t°$ C.

In the case of any isotropic substance it is easy to establish a relation between its coefficient of linear expansion and its coefficient of cubical expansion. Thus, if we consider any unit cube of the substance at $0°$ C., the length of its edge, which is 1 unit at $0°$ C., becomes $(1 + l)$ units at $1°$ C., where l is the coefficient of linear expansion of the substance. Similarly,

the volume of the cube, which is 1 cub. unit at 0° C., becomes $(1 + c)$ cub. units at 1° C., where c is the coefficient of cubical expansion of the substance. The volume of the cube is, however, also equal to $(1 + l)^3$ cub. units, so that,

$$1 + c = (1 + l)^3 = 1 + 3\,l + 3\,l^2 + l^3.$$

Now l is in all cases very small, so that l^2 and l^3 are negligibly small quantities,* we may therefore write

$$1 + c = 1 + 3\,l.$$

That is, $c = 3\,l$, or the coefficient of cubical expansion of any substance is approximately equal to three times its coefficient of linear expansion.

It is to be noted that a coefficient of expansion is the *ratio* of two lengths, and is, therefore, a number ; it is always small, and is usually expressed as a small decimal fraction.

15. Measurement of the Coefficient of Linear Expansion of a Solid.—The determination of the coefficient of linear expansion of a solid was the object of the earliest measurements made in the experimental study of expansion. It was thought at first that this was the proper starting point for the determination of the cubical expansion of solids and liquids. It was, however, recognised later, after the discovery of Dulong and Petit's method of determining the coefficient of cubical expansion of a liquid, that the determination of the coefficient of cubical expansion of a standard liquid, such as mercury, is the best starting point for this purpose.

The elaborate methods which have been adopted for the determination of the coefficient of linear expansion of a solid are of great historical interest, but they are now of little practical value, and need not here be considered.

The following simple methods, suitable for laboratory practice, sufficiently illustrate the character of the measurements to be made in a determination of this kind.

*Calculate the values of l^2 and l^3 in the case of glass for which $l = \cdot000008$.

Experiment 14.—The coefficient of linear expansion of a solid is very small, so that special methods have to be adopted for the accurate measurement of the change in length to be determined.

In this experiment the micrometer screw method is adopted. A micrometer screw is an accurately cut screw of small pitch, usually about half a millimetre, provided with a large circular head, which is divided round its circumference, as shown in the figure below, into 50 or 100 equal parts. As the screw is turned its point advances in the direction of its length, through a distance equal to its pitch for each complete revolution, so that if we can measure, by means of the divided head, to $\frac{1}{100}$ of a revolution, the movement of the point of the screw through a distance of $\frac{1}{200}$ mm. can be measured.

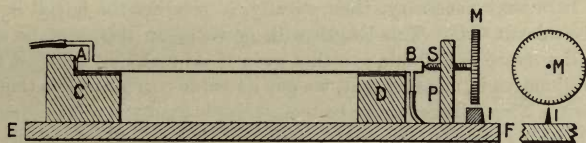Set up the apparatus shown diagrammatically in Fig. 18, for the

Fig. 18.

determination of the coefficient of linear expansion of the thin metal tube AB. The tube rests on two blocks, C and D, made of cork or wood, and mounted on a stout base board, EF. The end of the tube at A abuts on a face of the block C, but the end at B is free to move forward away from A as the tube expands.

The micrometer screw S is mounted in the pillar P with its axis in a line with the tube, so that its end can be brought into contact with the end of the tube at B. The end view of the divided head M, given in the small side figure, shows how the rotation of the screw can be read off on the divided scale by means of the small index fixed to the base board at I.

[A spherometer or a micrometer depth gauge may evidently be fixed in a clip at P in such a way as to take the place of the special screw and pillar arrangement here described.]

The tube is provided with two side tubes at A and B, so that it can be cooled to 0° C. by passing a stream of ice-cold water through it, and heated to 100° C. by passing a rapid current of steam through it. The tube should be protected from loss or gain of heat during these processes by wrapping it lightly round with strips of flannel. The tube being of metal, is of good conducting material, and may be assumed to take the temperature of the water and the steam if the current, in each case, is rapid enough, and is passed for a sufficiently long time. Tap water at its ordinary temperature may be used

instead of ice-cold water, but the temperature of the water must be determined.

When the apparatus is set up the course of the experiment is as follows. Pass the stream of water through the tube for some minutes, then adjust the screw until the end of it touches the end of the tube, and note the reading of the divided head opposite the index I. Repeat the reading once or twice to make sure that it is constant. Next turn the screw back clear of the tube, and pass a strong current of steam from a small boiler through the tube for some time. Then adjust the screw again into contact with the end of the tube, and read the divided head as before.

The difference of the two readings evidently gives with some accuracy the change in the length of the tube when heated from 0° C. to 100° C.

It is next necessary, theoretically, to measure the initial length of the tube at 0° C. This length will, however, in this case, be at least half a metre or 500 mm., so that even if we make an error of several millimetres in measuring it, we get its value correct to less than 1 per cent. This will generally be more correct than the value obtained for the change of length, so that it is quite unnecessary to try to obtain the correct initial length of the tube at 0° C. ; it is quite sufficient to measure the length of the tube carefully with a metre scale at the ordinary temperature.

In this, and similar experiments, the whole difficulty lies in getting an accurate measure of the change in the length of the rod ; the change is so small that a very small error in it may be a very large percentage error.

If, now, a denote the observed change in length corresponding to a rise of temperature from 0° C. to t° C., and L the length of the tube (at 0° C.), the mean value of l is given by $l = \dfrac{a}{\mathrm{L}t}$.

If the stream of cold water passed through the tube be at t'° C., instead of 0° C., and a denotes the change in length observed, the value of L is given by $l = \dfrac{a}{\mathrm{L}\,(t - t')}$, where L denotes theoretically the initial length at 0° C., not at t'° C. As explained above, however, the length of the tube measured in the ordinary way with a metre scale, at the ordinary temperature, is a sufficiently accurate value for the initial length whatever the initial temperature may have been.

The value of a, the observed change of length, will of course be different in the two cases given above, and the value of the result depends entirely on the accuracy with which a is determined.

Numerical Example.—In an experiment of this kind, with a

copper tube 502 mm. long, the reading of the screw-head when the tube was maintained at 10° C. by a stream of tap water, was 42 divisions; the reading when the tube was raised to 100° C. by a current of steam was 193 divisions. The pitch of the screw was known to be ·5 mm., and its head was divided into 100 divisions.

Here the change in the length of the tube for the rise of temperature from 10° C. to 100° C. is (151 × ·005) mm. or ·755 mm.

The coefficient of linear expansion is therefore given by

$$l = \frac{·755}{502 \times 90} = ·0000169.$$

That is, the coefficient of linear expansion is found by this experiment to be about ·000017.

A useful modification of the apparatus of this experiment which may be used for rods of any material not affected by water is shown in Fig. 19.
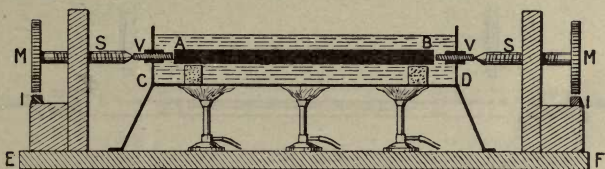
Fig. 19.

The rod AB is supported horizontally in a long rectangular metal trough, in which it can be surrounded with water at any temperature. Its ends abut on the ends of the two short rods of invar, shown at V, V, which are fitted loosely through two watertight stuffing-boxes in the ends of the trough. A micrometer screw is mounted at each end of the trough, so that its end can be brought into contact with the outer end of the invar rod adjacent to it.

The water (or oil) in the trough can be heated by blowing steam into it or by means of burners, as shown in the figure; and its temperature can be read at any time on a thermometer attached to the rod. The change in length corresponding to any known change in temperature, is deduced from the differences in the readings of the micrometer screws at the end of the rod. The expansion of the invar plugs at V is quite negligible, so that the change in the distance between the points of the two screws, as indicated by the changes in the readings of the screw-heads, gives directly the expansion of the rod.

Experiment 15.—Another method of measuring the small change in length which accompanies change of temperature depends

upon the use of a low power microscope. A scale of very small divisions, photographed on a small glass disc, is placed in the eyepiece of the microscope, so that on looking through the instrument the scale is seen in good focus across the circular field of view, which should be about a tenth of an inch in diameter. The value of these divisions is readily determined by focussing the microscope on a small photographic scale (a stage micrometer scale), showing divisions ·1 mm. in length. If, for example, 40 divisions of the eyepiece scale are found to coincide with 4 of the scale divisions, the value of each division of the eyepiece scale is evidently ·01 mm.

A determination of the coefficient of linear expansion of a rod of any material may be made by this method in the following way.

A rod, AB, mounted on cork supports, is enclosed, as shown in Fig. 20, in a wide glass tube, CD, provided with inlet and exit tubes at
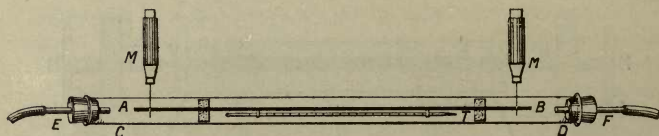
Fig. 20.

E and F. The temperature of the rod can be controlled by passing a current of water or steam through the tube CD, and its temperature is given at any time by the thermometer, T, attached to it.

Two microscopes, shown at M and M, are mounted vertically over the ends of the rod, so that each can be focussed on a fine line engraved on the rod near each end.

The position of this line on the eyepiece scale of each microscope can thus be read at any temperature, and the *change* in the distance between the two lines on the rod which corresponds to any known change in temperature, can be deduced directly from the differences in the readings of the positions of these reference lines on the eyepiece scales of the two microscopes. The distances between the two lines can be measured directly with a metre scale.

If the material of the rod is such that it cannot be exposed to water and steam, it should be enclosed, with the thermometer, in a glass tube, and the tube sealed.

16. **Table of Coefficients of Linear Expansion.**—The coefficients given below are the approximate values of the mean coefficients of linear expansion between 0° C. and 100° C.

In the case of substances of variable composition, only single representative values are given.

Platinum, ...	·0000089
Iron, ...	·000012
Nickel, ...	·000013
Gold, ...	·000014
Copper, ...	·000017
Silver,.	·000019
Aluminium, ...	·000023
Tin, ...	·000023
Lead, ...	·000029
Zinc, ...	·000029
Invar (nickel steel), ...	·000001
Cast iron, ...	·000011
Steel, ...	·000012
Bronze, ...	·000018
German silver, ...	·000018
Brass, ...	·000019
Porcelain, ...	·0000034
Gas carbon, ...	·0000054
Glass, ...	·0000084
Sulphur, ...	·00006
Vulcanite, ...	·00008

17. Cubical Expansion.—The coefficient of cubical expansion of a solid may be deduced from the value of its coefficient of linear expansion by the relation, $c = 3l$, established above. It has been explained in Art. 15 that this was the method originally adopted for the determination of this coefficient. The value of l was determined as accurately as possible by experiments, and the value of c given by $c = 3l$ was taken as its true value. It is found, however, that the coefficient of cubical expansion can be determined experimentally with much greater accuracy than the coefficient of linear expansion, and it is, therefore, preferable to determine c by experiment.

The experimental methods of determining the coefficient of cubical expansion of a solid involve, however, the determination

of the coefficient of cubical expansion of a liquid, and are, there-
fore, best considered in connection with the methods adopted in
the experimental study of the cubical expansion of liquids. The
cubical expansion of solids and liquids is in fact one subject, and
is so dealt with in the next chapter.

One result of the cubical expansion of any substance may,
however, be dealt with here. As a substance expands and its
volume increases, its density necessarily decreases. The mass of
the substance remains constant as it expands, and is given at
any temperature by the product of the volume and the density
at that temperature.

Hence, if v_o and d_o denote the volume and density at $0°$ C.,
and v_t and d_t the volume and density at $t°$ C., we have—

$$v_o \, d_o = v_t \, d_t,$$

that is,

$$\frac{d_o}{d_t} = \frac{v_t}{v_o}.$$

But,

$$v_t = v_o \, (1 + ct), \text{ or } \frac{v_t}{v_o} = 1 + ct,$$

where c denotes the coefficient of cubical expansion of the
substance. We therefore have—

$$\frac{d_o}{d_t} = 1 + ct,$$

or,

$$d_t = \frac{d_o}{1 + ct}.$$

This relation between the density at any temperature, $t°$ C., and
the density at $0°$ C., is true in this form for solids, liquids, and
gases. In the case of solids and liquids the value of c is small,
and the value of ct will generally be small enough to give
$\dfrac{1}{1 + ct}$ its approximate value $(1 - ct)$, and to write the relation
in the form—

$$d_t = d_o \, (1 - ct).$$

18. **Applications of Expansion.**—The force exerted by a solid against any constraint opposing its expansion or contraction in any direction is extremely great. This is well illustrated by the following experiment :—

Experiment 16.—A bar of iron, AB, Fig. 21, fits into slots in the iron uprights, CD, of the solid iron frame shown in the figure. The bar can be fixed between the uprights by inserting a short cast-iron pin, *b*, in the hole at the end, B, and then screwing up the screw nut at A.

The apparatus is intended to show the great force which the bar can exert in contracting.

The bar is heated nearly to redness, then quickly fixed in position by means of the pin at B and the screw nut at A.
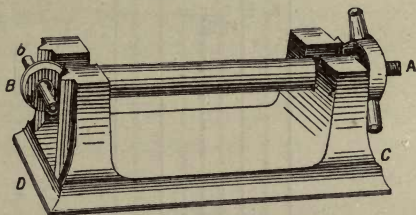
Fig. 21.

The screw nut is screwed up as tightly as possible, and the bar is then left to cool.

It will be found that in a few minutes the pin at *b* will snap suddenly in two under the stress exerted on it by the contracting bar.

The expansion and contraction of the materials used in construction of any kind may thus be a source of danger, and it is necessary in some cases to make special provision for it to take place without damage to the structure. This is specially the case where long lengths of any expansible material are used in situations where they are liable to considerable changes in temperature. Metal, on account of its expansibility and rigidity, is specially troublesome under these conditions.

Thus, in building construction, beams and girders, particularly iron beams and girders, are fixed so as to be free to expand and contract without damage to the walls. In laying a railway the

4

rails are laid in *chairs*, in which they are free to expand and
contract, and a small gap is left between the ends of adjacent
rails for the same purpose. This is a case of special import-
ance, for a single rail may change in length by nearly half an
inch as the result of the changes of temperature to which it is
exposed. If, therefore, the rails were rigidly fixed and in
contact at the ends, the line would be broken and twisted by
the force exerted by the rails in expanding and contracting.
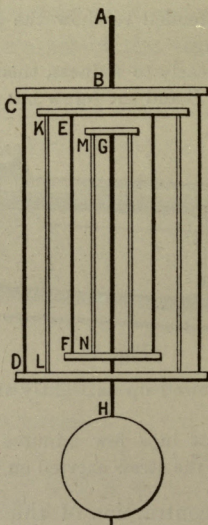
Fig. 22.

Again, in building iron bridges similar precautions have to be
taken. In the tubular suspension bridge over the Menai Straits,
for example, the main girders of the bridge rest on rollers at
each end so as to be free to expand or contract with change of
temperature.

In the construction of reliable clocks and watches, special
means have to be taken to compensate for the expansion and
contraction of the time-keeping parts of the mechanism. In

the case of a clock controlled by a pendulum, the rate of going depends upon the "length" of the pendulum, the "length" being measured from the point of suspension of the pendulum to a point at the lower end, known as the centre of oscillation of the pendulum. The clock goes fast when this length increases, and slow when it decreases. The clock, therefore, gains as the temperature rises, and loses as the temperature falls, unless some device is adopted to prevent the length of the pendulum from changing with change of temperature.

Harrison's compensating pendulum, or gridiron pendulum, is the best known of these devices. In this pendulum, shown in Fig. 22, the bob is carried, not by a single rod, but by a framework of rods arranged in two sets, so that the upward expansion of one set of rods exactly compensates for the downward expansion of the other set.

It will be seen from Fig. 22 that the expansion of the rods shown in thick lines lowers the bob and increases the length of the pendulum, while the expansion of the rods shown in thin lines raises the bob and decreases the length of the pendulum. If, therefore, the upward expansion of the one set of rods raises the centre of oscillation by the same amount as the downward expansion of the other set lowers it, the "length" of the pendulum will be constant, and the rate of the clock will be constant. It will be seen, however, that the rods indicated by the thin lines are necessarily shorter than the other set; they must, therefore, be made of more expansible material than the other rods, in order that they may give the same total expansion for the same rise of temperature. In Harrison's pendulum the rods were made of steel and brass, the shorter rods being made of brass, the more expansible metal.

In designing the pendulum for any two metals, it would evidently be necessary to arrange for the lengths of the compensating rods in the two metals to be inversely proportional to the coefficients of linear expansion of the metal. Thus in

Fig. 22 the lengths (AB + CD + EF + GH) and (KL + MN), are the compensating lengths in steel and brass, and if L_1 and L_2 denote these lengths respectively, and l_1 and l_2 denote the coefficients of linear suspension of steel and brass respectively, then, for exact compensation, we must have

$$\frac{L_1}{L_2} = \frac{l_2}{l_1}.$$

In the case of steel and brass the ratio l_2/l_1 is approximately equal to 3/2, so that the compensating lengths of steel and brass rods must be approximately in the ratio 3 : 2.
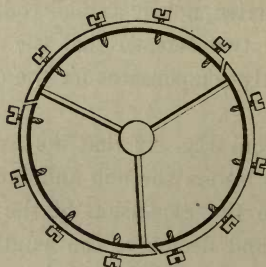
Fig. 23.

Graham's mercury pendulum is another form of compensating pendulum. In this pendulum the bob is arranged to carry one or two glass cylinders partly filled with mercury. The quantity of mercury in the cylinders is adjusted so that the centre of oscillation of the pendulum is raised by its expansion through the same distance as it is lowered by the expansion of the rod.

In clocks, chronometers, and watches which are controlled by balance wheels, the rate of going depends upon the *radius of gyration* of the wheel, and also upon the strength of the hair-spring which actuates the wheel. The greater the radius of gyration, and the weaker the spring, the slower is the rate of going. When the temperature rises the wheel expands, and its radius of gyration increases; at the same time the elasticity of

the material of the hairspring decreases, and the spring, therefore, becomes weaker. It follows from this that unless provision is made for compensation, a time-keeper controlled by a balance wheel, goes slow when the temperature rises, and fast when the temperature falls.

The usual method of compensation involves a special construction of the rim of the wheel. The rim is divided, as shown in Fig. 23, into three or more sections, each carried by a spoke of the wheel. Each section is made of two strips of metal of different expansibility, soldered together with the less expansible metal on the inner side; it also carries several small compensating masses screwed into it.

When a balance wheel constructed in this way expands, the spokes increase in length, and carry the sections of the rim attached to them outwards; at the same time each section bends inwards, and so brings the compensating weights nearer to the centre of the wheel. It is, therefore, possible by a proper distribution of these weights to compensate exactly for the disturbing effects of change of temperature.

The great force exerted by a solid body in contracting has some interesting applications.

The iron tyres of cart and waggon wheels are put on while they are red hot; they then fit easily over the wooden rim, but as they contract they bind the whole wheel firmly together, and when cool they fit tightly round the rim. In the same way boiler plates are rivetted with red hot rivets, which contract with such force in cooling that they draw the plates closely enough together to form a steam-proof joint.

19. Breguet's Metallic Thermometer.—Several thermomometers, based on the expansion of metals, have been constructed at different times. Breguet's thermometer, shown in Fig. 24, is the best known instrument of this type.

It consists essentially of a long spiral made of three thin strips of silver, gold, and platinum, rolled together with the

gold in the middle, so as to form a thin ribbon-like strip, which is coiled into a spiral with the most expansible metal, silver, on the inner side. It will be seen that by this construction the spiral unwinds as the temperature rises, and coils up as the temperature falls.

The spiral is suspended vertically, as shown in the figure, over the centre of a horizontal circular scale, and carries at its lower end a horizontal pointer which moves, as an index, round the scale.
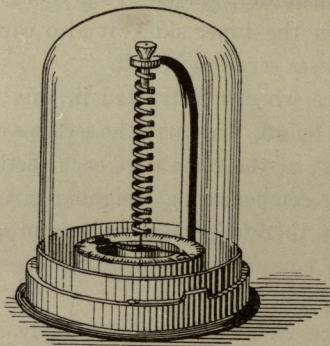
Fig. 24.

As the temperature changes the spiral winds up or unwinds, and the corresponding motion of the pointer round the scale indicates the nature and extent of the changes of temperature.

The instrument is of little practical use. It is, however, very sensitive to small changes of temperature, and may be used conveniently to give an automatic record of the changes of temperature, and to indicate the maximum and minimum temperatures during any given period. It has also been adapted recently to form the indicating part of an instrument used for measuring very high temperatures.

CHAPTER IV.

EXPANSION OF LIQUIDS.

20. Expansion of Liquids.—The study of the expansion of liquids is complicated by the expansion of the containing vessel. When a liquid is heated in any vessel the liquid and the vessel both expand, and the expansion observed is not the *real* expansion of the liquid, but the difference between the expansion of the liquid and the increase in the capacity of the vessel. If the expansibilities of the liquid and the material of the vessel were equal there would be no apparent expansion, for the increase in the capacity of the vessel would be exactly equal to the increase in the volume of the liquid. If, however, the liquid is more expansible than the material of the vessel it appears to expand, but if it is less expansible, then it appears to contract. Liquids are in general much more expansible than solids, so that when a liquid is heated in a glass vessel it, in general, appears to expand, but it must be remembered this *apparent* expansion is really the difference between the real expansion of the liquid and the increase in the capacity of the vessel, as seen in the expanded vessel.

Experiment 17.—Fix up a small expansion flask as shown in Fig. 2 and described in Exp. 2. Place some hot water in a large beaker and immerse the flask suddenly in this water. Note carefully in doing this how the level of the liquid in the stem of the flask behaves.

It will be found that the column at first falls for a few seconds and then rises.

The fall is due to the fact that the flask is first heated and expands slightly before the liquid in it begins to expand.

Liquids like solids differ in expansibility. This fact is con-
veniently illustrated by the following experiment.

Experiment 18.—Fit up four small flasks of exactly the same
capacity in the manner indicated in Fig. 2, and explained in
Exp. 2. Fill the flasks with water, glycerine, alcohol, and ether
respectively, so that the liquid stands at the same level in the stem
in each flask. Then place the flasks in the same water bath as shown
in Fig. 25. The flasks are conveniently fixed in the bath by fitting
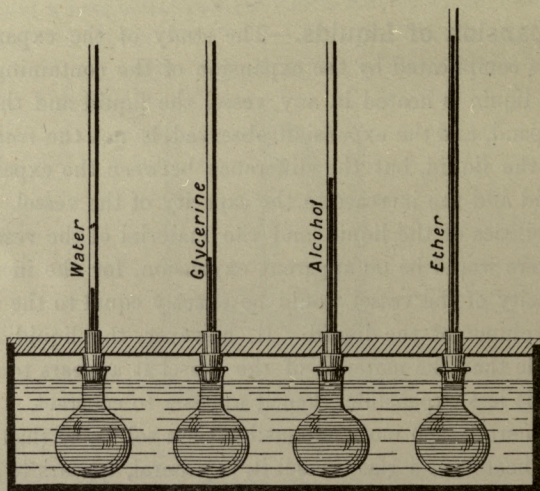
Fig. 25.

the stems with corks into holes in a stout wooden cover placed over
the bath, as shown in the figure.

Now heat the water in the bath slowly from about 10° C. to 25° C.,
and notice the expansion of the liquid in each flask as the temperature
rises. The water in the bath should be stirred during heating so as
to secure uniformity of temperature throughout its mass.

It will be seen that the liquids expand through very different
amounts for the same rise of temperature. The ascending order of
expansibility should be found to be water, glycerine, alcohol, ether ;
and their relative apparent expansions for the same rise of tempera-
ture should be roughly in the ratio 1 : 3 : : 6 : 12.

The expansion of the flask is the same for each liquid, and does not, therefore, alter the general result of the experiment.

This experiment can be carried out by testing different liquids successively in the same flask and noting the expansion in each case.

The question as to whether a liquid expands by equal amounts for each degree rise of temperature, as indicated by a mercury-in-glass thermometer, is readily investigated by the method indicated in the following experiment.

> **Experiment 19.**—Take an expansion flask, similar to those used in the foregoing experiment, and fill it carefully with alcohol, or any other convenient liquid. Attach a scale of some kind to the stem of the flask so that the level of the column of liquid in the stem can be conveniently read on it. A stiff paper scale graduated in millimetres, and attached to the stem in the manner indicated in Fig. 26 will serve.
>
> Place the flask in a water bath and heat it gently from 0° C. to about 50° C. As the temperature rises read the level of the column in the stem at a number of temperatures differing by about 5°, taking care to stir the water well before taking each reading.
>
> It will be found that in the case of most liquids the increase in volume is not directly proportional to the rise in temperature.
>
> In general, the amount of expansion for each degree rise of temperature increases as the temperature rises.

Fig. 26.

This result, as in the case of solids, merely means that all liquids do not obey the same law of expansion as mercury. The result may be concisely stated by saying that liquids do not in general expand uniformly with rise of temperature *as indicated by a mercury-in-glass thermometer.*

21. **Apparent Expansion.**—The apparent expansion of a liquid in a vessel is the expansion which appears to take place when the liquid and the vessel are heated together and undergo the same change of temperature.

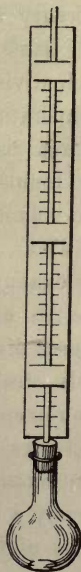Thus, if the volume of a liquid in a graduated glass vessel is

given *by the graduations on the vessel* to be n units at $t°$ C., and n' units at a higher temperature, $t'°$ C., then $(n' - n)$ units is the *apparent expansion* between $t°$ C. and $t'°$ C. This, however, is not the *real expansion* of the liquid, for the capacity of each unit of volume is obviously not the same at the two temperatures; it is greater at $t'°$ C. than at $t°$ C. on account of the expansion of the vessel between these temperatures.

The temperature scale of a mercury-in-glass thermometer evidently depends upon the *apparent* expansion of mercury in a glass tube. In graduating the thermometer the bore of the stem is divided into equal divisions. The expansion of the mercury for each degree rise of temperature is thus *apparently* the same, but it must be remembered that the volume of each division increases with the expansion of the tube as the temperature rises. The *real* expansion of the mercury for each degree rise of temperature therefore increases very slightly as the temperature rises, and is for any particular degree equal to the volume of the degree division at the temperature at which it is filled. The real expansion of the mercury from $0°$ C. to $1°$ C., for example, is the volume of the degree division at $1°$ C., while the real expansion from $99°$ C. to $100°$ C. is the volume of the degree division at $100°$ C.

In dealing with apparent expansion quantitatively, it must be remembered that the capacity of a vessel of any material increases in volume in exactly the same way as if it were a continuous block of the material. A glass flask, for example, is merely a block of glass with a large cavity in it, and the dimentions of the cavity increase with rise of temperature in exactly the same way as they would if it were filled with solid glass.

The **coefficient of apparent expansion** of a liquid in any vessel may be defined as the ratio of the apparent increase in volume per degree to the initial apparent volume at $0°$ C. Thus if n denotes the apparent volume of a liquid at $0°$ C. and n' its apparent volume at $t°$ C., then the mean coefficient of apparent

expansion between $0°$ C. and $t°$ C. is given by

$$a = \frac{(n' - n)}{nt},$$

or $n' = n\,(1 + at)$

That is, if a denote the mean coefficient of apparent expansion of a liquid between $0°$ C. and $t°$ C., then one unit of volume at $0°$ C. becomes apparently $(1 + at)$ units at $t°$ C., and n units at $0°$ C., therefore, becomes apparently $n\,(1 + at)$ units at $t°$ C. Hence, we write

$$n' = n\,(1 + at)$$

The relation between the coefficient of real expansion of a liquid and its coefficient of apparent expansion in a vessel of any material may be obtained simply as follows.

Let the apparent volume of a liquid in a graduated glass vessel be n units at $0°$ C. and n' units at $1°$ C., then, as above, the coefficient of apparent expansion is given by

$$a = \frac{n' - n}{n}.$$

Now each unit of volume increases with the expansion of the glass vessel, so that 1 unit at $0°$ C. has a real volume of $(1 + g)$ unit at $1°$ C., where g denotes the coefficient of cubical expansion of the glass. If, therefore, the real volume of the liquid at $0°$ C. be taken as n units, its real volume at $1°$ C. is $n'\,(1 + g)$ units, the units here being the same at both temperatures. The coefficient of real expansion of the liquid is thus given by

$$c = \frac{n'\,(1 + g) - n}{n}.$$

That is,

$$c = \frac{n' - n + n'g}{n};$$

or

$$c = \frac{n' - n}{n} + \frac{n'}{n}\,g.$$

Now $\dfrac{n' - n}{n} = a$, and $\dfrac{n'}{n}$ in the term $\dfrac{n'g^*}{n}$ may be taken as 1 ; we, therefore, have

$$c = a + g.$$

That is, the coefficient of real expansion of the liquid is approximately equal to the sum of the coefficient of apparent expansion and the coefficient of cubical expansion of the material of the vessel.

It will be found that this relation is of great practical importance in the experimental study of the cubical expansion of liquids and solids.

22. Methods of Determining the Coefficient of Apparent Expansion of a Liquid.—The mean coefficient of apparent cubical expansion of a liquid between any two temperatures can be determined experimentally by three important methods.

The Dilatometer Method.—The dilatometer,[†] shown in Fig. 27, is merely a large bulb tube, like a large thermometer tube, with a stem graduated in divisions of equal volume. The tube is filled with the liquid up to a convenient division on the stem at $0°$ C., and its apparent volume, as indicated by the graduations, noted. It is then heated to $t°$ C., and its apparent volume again noted. Then, if n units denote the observed volume at $0°$ C., and n' units the observed volume at $t°$ C., the coefficient of apparent expansion is given by

$$a = \frac{n' - n}{nt}.$$

[*] The ratio $\dfrac{n'}{n} = 1 + a$, so that $\dfrac{n'}{n} g = (1 + a) \, g = g + ag$. Now a and g are both *very small*, so that ag is negligibly small and may, therefore, be neglected.

[†] A more convenient form of this instrument is a U-shaped form in which the bend or the lower portion of one limb of the tube forms the bulb, and each limb is continued upwards as a capillary stem. A zero index mark is engraved on one stem and a scale on the other. This form of dilatometer is very easily filled and cleaned, and is quite as convenient and accurate in use as the form described above.

It must be noticed that, in order that it may be possible to read off the apparent volume of the liquid at any temperature, the capacity of the bulb up to the zero of the scale on the stem must be known in terms of the stem divisions. This capacity is readily determined by comparing the mass of mercury which fills the bulb and stem up to the zero of the scale, with the mass which fills one division of the stem.

The practical details of this method of determining the coefficient of apparent cubical expansion of a liquid are briefly indicated in the following experiment.

Experiment 20.—First standardise the dilatometer tube by determining the capacity of the bulb up to the zero on the stem in terms of the scale divisions. Pour a *small* quantity of mercury into the funnel, and get a fairly long thread of mercury into the tube by slightly warming the bulb and then allowing it to cool as in filling a thermometer tube. Pour away the excess of mercury in the funnel; then measure the length of the thread in the stem in stem divisions, run it out into a small crucible, and weigh it. Find from these data the mass of mercury which fills one division of the stem, and let this mass be denoted by m.

Now fill the bulb and stem with mercury up to any convenient point on the stem. Some hours (better, days) after, when the mercury and bulb are cool, and at the same temperature as in the first part of this determination, read the level of the mercury thread in the stem; then weigh the mercury in the tube, and calculate from these data (and the value of m above) the mass of mercury which fills the bulb and stem up to the zero of the scale. Let this mass be denoted by M.

The capacity of the bulb up to the zero is thus determined as equal to M/m scale divisions.

Fig. 27.

This determination can, obviously, be made, once for all, for a given tube, and should, for convenience of reference, be engraved on the tube.

When the tube is standardised in this way the process of determining the coefficient of apparent expansion of any liquid with it is as follows.

Fill the tube with the liquid. (In Laboratory practice it is convenient to take mercury as the liquid, if the tube has been standardised, for when this process is over the tube is full of mercury ready for the expansion part of the experiment.)

Then place the tube first in melting ice, and then in steam from boiling water (exactly as described in Art. 8, with reference to the determination of the fixed points of a thermometer), and note the reading of the level of the liquid in the stem in each case.

Let these readings be n divisions at 0° C., and n' divisions at 100° C., then a, the coefficient of apparent expansion, is given by

$$a = \frac{n' - n}{100\ n}.$$

23. The Weight Thermometer Method.

The usual form of the weight thermometer is shown in Fig. 28. It is a tube with a large cylindrical bulb about 5 cms. long, and 1 cm. in diameter, provided with a short stem of small bore bent into the form shown in the figure, and drawn out to a fine point at the end.
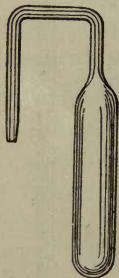
The tube is filled with the liquid at 0° C., then heated to a known temperature, $t°$ C., and the liquid which overflows as the result of the expansion caused by the rise of temperature is collected in a crucible and weighed. When the overflow is complete, the weight of the liquid left in the tube is determined by weighing when the tube is cool.

Fig. 28.

The liquid which remains in the tube during the heating from 0° C. to $t°$ C.—that is, the liquid which is left in the tube after the experiment is over—expands during the rise of temperature from 0° C. to $t°$ C., so as to displace the liquid which has overflowed, and so fill the tube at $t°$ C. The apparent expansion of this liquid between 0° C. and $t°$ C. is therefore the volume which the overflow occupied at 0° C.

Hence, if w denote the weight of the liquid which overflows, and W the weight which remains in the tube after the overflow is complete, and the ratio of the apparent expansion between 0° C. and $t°$ C. to the initial volume at 0° C. is $\frac{w}{W}$, for the

volumes occupied by these weights in the tube at the initial temperature are proportional to the weights. The mean co-efficient of apparent expansion between 0° C. and $t°$ C. is, there-fore, given by $a = \dfrac{w}{Wt}$.

A convenient method of carrying out a determination of the mean coefficient of apparent cubical expansion of a liquid by this method is given in the experiment described below.

Experiment 21.—First weigh the weight thermometer tube care-fully and record the weight. Adjust a pad of asbestos wool round the stem of the tube, a little above the bulb, and fix it by means of this pad in a clamp at a small angle with the vertical. Place a quantity of the liquid whose coefficient of apparent expansion is to be determined in a small beaker or large crucible, and adjust the vessel in position so that the end of the delivery tube of the ther-mometer dips below the surface of the liquid.

Now fill the tube with the liquid by alternate heating and cooling as described in Exp. 4. Care must be taken at this stage to heat the liquid in the beaker as well as the liquid in the tube ; otherwise the cold liquid entering the hot tube will break it.

When the tube is quite full of the liquid, and free from air bubbles, it is allowed to cool with the end of the tube below the surface of the liquid. Then, when the tube and liquid have cooled to the ordinary temperature, a tall beaker or jar is placed round the tube (without raising the end of it out of the liquid) and filled with small pieces of melting ice, which are piled round the tube until it is completely surrounded with melting ice at 0° C. The tube is allowed to stand for some minutes at this temperature, so that it may fill with the liquid at 0° C. It is then removed, and a small clean weighed crucible or beaker is placed under the open end so as to catch the overflow which begins as soon as the tube is taken out of the ice. The tube is then placed in a steam heater, similar to that shown in Fig. 8, and heated to 100° C. Care must be taken to collect the overflow without loss during this rise of temperature.

If the liquid has too low a boiling point to be heated to 100° C., it should be heated to a suitable temperature by immersing the ther-mometer tube in warm water in a large beaker.

Now weigh the crucible containing the overflow, and find the weight of the overflow by deducting the weight of the crucible. Let this weight be denoted by w. Then, when it is quite cool, weigh

the thermometer tube with the liquid left in it and find the weight of
this liquid by deducting the known weight of the tube. Let this
weight be denoted by W.

Then, as explained above, we have

$$a = \frac{w}{100\,W}.$$

24. Matthiessen's Density Method.

A very important
method of determining the coefficient of apparent cubical
expansion of a liquid is the density method adopted by
Matthiessen in his study of the expansion of water.

A solid sinker of convenient weight is weighed in the liquid
at $0°$ C. and at $t°$ C., and the apparent loss of weight noted in
each case. The apparent loss of weight at each temperature is,
by the principle of Archimedes, the weight of the displaced
liquid at that temperature. Then, if w_o and w_t denote the
apparent loss of weight at $0°$ C. and $t°$ C. respectively, then
w_o and w_t denote also the weight of the displaced liquid at
$0°$ C. and $t°$ C. respectively, and *since the volume of the displaced
liquid is apparently* * *the same at both temperatures*, the *apparent*
density of the liquid at these temperatures is proportional to
these weights. That is, if δ_o and δ_t denote respectively the
apparent densities of the liquid at $0°$ C. and $t°$ C., then

$$\frac{\delta_o}{\delta_t} = \frac{w_o}{w_t}.$$

But the mean coefficient of apparent cubical expansion of the
liquid between $0°$ C. and $t°$ C. is given (as in Art. 17) by

$$a = \frac{\delta_o - \delta_t}{\delta_t}.$$

Hence we have

$$a = \frac{w_o - w_t}{w_t t}.$$

---

* It will be noticed that the *apparent expansion* is in all cases the
observed expansion *uncorrected* for the expansion of the containing vessel
or, as in this case, the displacing solid.

A convenient method of making a determination by this method is outlined in the experiment described below.

Experiment 22.—Set up a balance on a shelf or table some feet above the level of a laboratory bench. Then suspend a suitable glass sinker from the under side of one pan of the balance by a long silk fibre, which passes through holes in the bottom of the balance case and in the table or shelf on which the balance stands. The
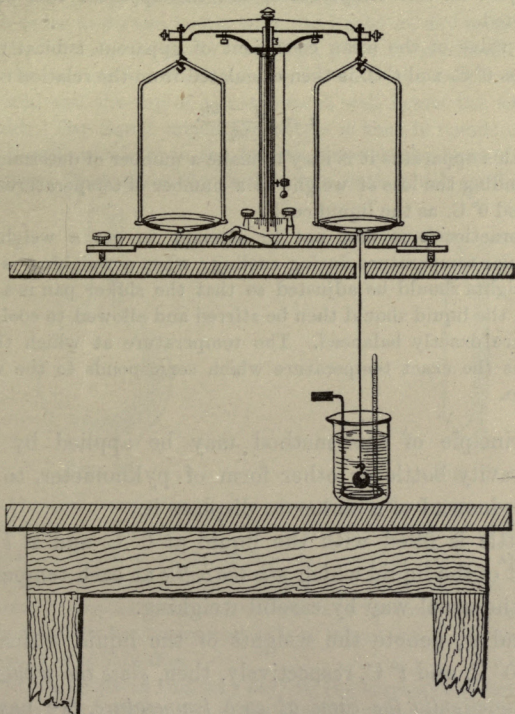

Fig. 29.

liquid is placed in a beaker on the bench below the balance, and the length of the fibre carrying the sinker is adjusted so as to allow the sinker to hang freely in the liquid when the beam of the balance is free

Fig. 29 gives a general view of the arrangement of the apparatus.

The sinker is first carefully weighed (in air) and its weight noted.

The liquid is then reduced to 0° C. by surrounding the beaker containing it with ice in a larger vessel. When the thermometer in the liquid indicates that its temperature is fixed at 0° C., the sinker is weighed in the liquid, and the apparent loss of weight, w_o, noted. The liquid is then raised to some other suitable temperature, $t°$ C., either by directly heating it or by surrounding the beaker containing it with hot water in a larger vessel. The sinker is weighed in the liquid at this temperature, and the apparent loss of weight, w_t, noted.

The value of the mean coefficient of apparent cubical expansion between 0° C. and $t°$ C. is then calculated from the relation :—

$$a = \frac{w_o - w_t}{w_t}.$$

With this apparatus it is easy to make a number of determinations of a by finding the loss of weight at a number of temperatures between $t°$ C. and 0° C. as the liquid cools.

In practice it is best not to attempt to get a weighing at a particular temperature during cooling ; when a weighing is required the weights should be adjusted so that the sinker pan is a little too heavy, the liquid should then be stirred and allowed to cool until the pans are exactly balanced. The temperature at which this takes place is the exact temperature which corresponds to the weight in the pan.

The principle of this method may be applied by using a specific gravity bottle or other form of pyknometer, to contain the liquid, instead of a sinker to displace it.

The bottle is filled with the liquid at 0° C. and at $t°$ C., and the weight of the liquid which *fills the bottle* at each temperature is found in the usual way by careful weighing.

If w_o and w_t denote the weights of the liquid which fill the bottle at 0° C. and $t°$ C. respectively, then, *since the volume of the liquid is apparently the same at each temperature*, we have, as in the case of the liquid displaced by the sinker,

$$\frac{\delta_o}{\delta_t} = \frac{w_o}{w_t}.$$

And the mean coefficient of apparent cubical expansion of the liquid between 0° C. and $t°$ C., is given by

$$a = \frac{w_o - w_t}{w_t t}.$$

A determination of the coefficient of apparent expansion of a liquid may be made with an ordinary specific gravity bottle by the method described in the following experiment.

Experiment 23.—See that the specific gravity bottle is clean and dry; then weigh it, and note the weight.

In order to fill the bottle with the liquid at any temperature, first fill the bottle in the usual way, then place it in a small beaker and fill the beaker up with the liquid until the bottle is completely covered and the top of the stopper is well below the surface of the liquid. The liquid inside the bottle is thus in communication with the liquid outside it in the beaker, through the bore of the tubular stopper. Now place the beaker in a bath which can be adjusted to

Fig. 30.
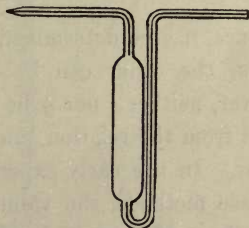
Fig. 31.

the required temperature, and after this temperature has been maintained for a sufficiently long time, lift the bottle out of the beaker by means of a piece of platinum wire or thread previously attached to it.

When the temperature at which the bottle is filled is below the ordinary temperature of the room, it is necessary to place the bottle in a clean dry beaker as soon as it is taken out of the beaker and to weigh it in this beaker.

Fill the bottle in this way at 0° C. (by surrounding the beaker with melting ice), and at any other suitable temperature, $t°$ C., and find the weight of the liquid which fills the bottle at each temperature.

Then, if w_o and w_t denote the weights found in this way at 0° C. and $t°$ C., the mean coefficient of apparent cubical expansion of the liquid between 0° C. and $t°$ C. is given by

$$a = \frac{w_o - w_t}{w_t t}.$$

If a pyknometer of the form shown in Fig. 30 is used in this experi-

ment instead of the ordinary form of specific gravity bottle, it is easily filled with the liquid at any temperature by simply placing it full of liquid in the bath, and adjusting the level of the liquid with a pipette to the index ring at the required temperature.

In the case of a volatile liquid a pyknometer of the form shown in Fig. 31 should be used.

It will be seen from what has been said above, that the coefficient of apparent expansion of a liquid can be determined with great accuracy by any one of the methods here described, Now, if c denote the coefficient of *real* expansion of the liquid, and g the coefficient of cubical expansion of the material of the containing vessel or the displacing solid, as in Matthiessen's method, then, as explained in Art. 21, we have

$$a = c - g.$$

Hence, if a be determined by experiment, and either c or g be known, the other can be determined from this relation. If, however, neither c nor g be known, then neither can be determined from the relation, and the value found for a is practically useless. In the early experiments on the expansion of liquids by these methods, the value of g was generally taken as three times the coefficient of linear expansion of the material of the vessel. This value of g is not, however, sufficiently accurate for the purpose.

It was not until Dulong and Petit invented a method of determining the coefficient of real expansion of a liquid without involving the coefficient of expansion of the material of the vessel that a satisfactory way was found out of this difficulty.

Dulong and Petit in 1817, and Regnault later, in 1852, determined the coefficient of real expansion of mercury with great accuracy by this method. The value of c for a standard liquid was thus known, and could be used as a starting point in all apparent expansion methods.

25. The Determination of the Coefficient of Real Expansion of Mercury by the Method of Dulong and

Petit.—The principle of the method adopted by Dulong and Petit for the determination of the coefficient of real expansion of mercury is comparatively simple.

Imagine the limb AB of the tube ABCD, in Fig. 32, filled with a liquid of density d_1, and the limb CD with a liquid of density d_2, and that the liquids either meet in the horizontal branch BC, or are separated by a bubble of air in that branch.

Then, if h_1 and h_2 denote the heights of the columns in the limbs AB and CD, respectively, when the liquids are in hydrostatic equilibrium, the pressures in the branch BC, due to the
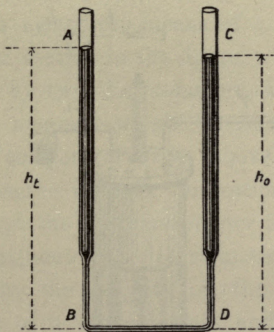
Fig. 32.

columns in AB and CD, are given by $h_1 \, d_1 \, g$, and $h_2 \, d_2 \, g$ respectively, and since the columns are in equilibrium these pressures must be equal. That is,

$$h_1 \, d_1 \, g = h_2 \, d_2 \, g,$$
or, $$h_1 \, d_1 = h_2 \, d_2.$$

This result gives a relation between the heights of the columns and the densities of the liquids, which is evidently quite independent of the dimensions of the tube.

If, therefore, the tube ABCD be filled with mercury in both limbs, and one limb is maintained at $0°$ C., while the other is maintained at $t°$ C., the heights of the columns in the limbs

necessary for hydrostatic equilibrium will be such that if h_o denote the height of the column at 0° C., and h_t the height of the column at t° C., we have—

$$h_o \, d_o = h_t \, d_t.$$

That is,

$$\frac{h_t}{h_o} = \frac{d_o}{d_t}.$$

But,

$$\frac{d_o}{d_t} = 1 - ct \quad \text{(Art. 17)}.$$

Therefore,

$$\frac{h_t}{h_o} = 1 - ct,$$

or,

$$c = \frac{h_t - h_o}{h_o t}.$$
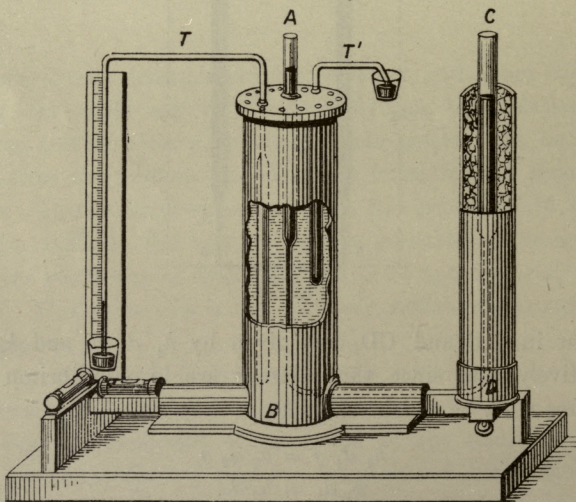
Fig. 33.

Hence, if ($h_t - h_o$) and h_o be measured carefully by appropriate methods, the value of c, the mean coefficient of *real* expansion of mercury between 0° C. and t° C., can be determined accurately by a method which is quite independent of the expansion of the tube.

The general arrangement of the apparatus adopted by Dulong and Petit is shown in Fig. 33. A tube of the form shown by ABCD in Fig. 33 was used. The bore of the horizontal branch was narrow to prevent transfer of heat from one limb to the other. The limb AB of the tube containing the mercury was surrounded by a copper cylinder, which served as an oil bath for heating the mercury in that limb to any desired temperature.

The limb CD was also enclosed in a cylinder and completely surrounded with melting ice, so that its temperature was maintained uniformly at 0° C.

The oil bath was heated by means of a small furnace built round it, as shown in section in the figure. The temperature of the bath was given by two thermometers, an air thermometer, T (Art. 32), and a mercury weight thermometer, T'. It was found that as the temperature rose above 100° C. the thermometers did not agree in their indications, so Dulong and Petit decided to adopt the air thermometer for the measurement of temperature throughout their determination.

The difference in the heights of the two columns was measured by means of a vertical scale and a telescope. The scale was engraved on a rod of steel or brass, and the telescope, with its axis horizontal, was mounted on the rod so that it could be moved up and down as required, and the extent of its motion accurately measured by the scale on the rod. In measuring the difference in the heights of the two columns the position of the telescope on the rod was adjusted, so that when focussed on the top of one of the mercury columns the horizontal cross wire in the field of view was seen to be tangential to the curved top of the column. The position of the telescope on the vertical scale was then read, and the reading recorded. The telescope was then raised or lowered so that it could be focussed in the same way on the top of the other column, and the reading of its position on the scale again taken. The

difference of these two readings gave the required difference in the heights of the two columns.

The height of the column at 0° C. was found by measuring in the same way the distance of the level of the column above or below a reference mark at a known distance above the axis of the horizontal branch of the mercury tube.

Dulong and Petit found the mean coefficient of real expansion of mercury between 0° C. and 100° C. to be ·0001818.

Some years later Regnault made a number of important improvements in the apparatus used by Dulong and Petit, and gave ·0001815 as a more accurate value of this coefficient. Regnault's value is the value now generally accepted.

Both Dulong and Petit and Regnault found that the expansion of mercury per degree rise of temperature *on the air thermometer* increases as the temperature rises.

It should be noted that this method of determining the coefficient of real expansion of a liquid is not suited for general use.

It is, rather, a standard method by which, as the result of a careful and troublesome research, the coefficient of a standard substance, such as mercury, can be accurately determined once for all.

26. General Method of Determining the Coefficient of Real Expansion of a Liquid.

—If we take Regnault's value of the coefficient of real expansion of mercury as a starting point, the coefficient of real expansion of any other liquid may be determined by any one of the apparent expansion methods described above. The general method of making a determination of this kind is briefly as follows :—

The coefficient of *apparent* expansion of mercury is first determined, either by the dilatometer method, or the weight-thermometer method. This gives the value of the coefficient of cubical expansion of the material of the vessel, for in the relation, $a = c - g$, or $g = c - a$, the value of c is known from

Regnault's results, and the value of a is given by the experiment. The value of g is thus determined accurately for the material of the particular tube used in the experiment.

The coefficient of *apparent* expansion of the liquid is next determined by the same method, using *the same tube* as was used in the determination of the apparent expansion of mercury. The value of c for the liquid is then given at once by the relation, $c = a + g$, for the value of a is given by this determination, and the value of g is known from the result of the mercury determination.

Either the dilatometer method or the weight-thermometer method must be used for the determination of the coefficient of apparent expansion of mercury; but Matthiessen's method can be used for the determination of the coefficient of expansion of the liquid. When the value of g for the dilatometer tube or weight-thermometer tube is found, a quantity of mercury sufficient to sink the tube in the liquid can be left in it, and the bulb can then be fused off and converted into a sinker, as shown in Fig. 34, suitable for use in a determination of the coefficient of apparent expansion of the liquid by Matthiessens' method.

Fig. 34.

Table of Mean Coefficients of Real Expansion of Liquids.

Water,	.	.	. ·00015	(10° C. to 20° C.)
Mercury,	.	.	. ·0001815	(0° C. to 100° C.)
Glycerine,	.	.	. ·00053	(0° C. to 30° C.)
Aniline,	.	.	. ·00091	(0° C. to 30° C.)
Oil of turpentine,		.	. ·00095	(0° C. to 30° C.)
Alcohol,	.	.	. ·00108	(0° C. to 30° C.)
Carbon bisulphide,		.	. ·00120	(0° C. to 30° C.)
Chloroform,	.	.	. ·00138	(0° C. to 30° C.)
Ether,	.	.	. ·00161	(0° C. to 30° C.)

27. **General Method of Determining the Coefficient of Cubical Expansion of a Solid.**—The coefficient of cubical expansion of a solid is best determined by Matthiessen's method of determining the coefficient of apparent expansion of a liquid.

A liquid suitable for studying the expansion of the given solid is selected, and its coefficient of *real* expansion is carefully determined by one of the methods described in the foregoing article. A piece of the solid is then used as a sinker, and the coefficient of apparent expansion of the liquid is determined. In this way the values of c and a in the relation, $g = c - a$, are found, and the value of g is therefore determined.

The dilatometer and weight-thermometer methods can also be used for finding the coefficient of cubical expansion of a solid by enclosing a piece of the solid in the bulb of a tube specially constructed for the purpose. The method is, however, a troublesme one, both in theory and in practice.

28. **The Expansion of Water.**—The expansion of water is of special interest and importance. It has received special attention in experimental research, not only because it exhibits a noteworthy peculiarity, but because water is selected as the standard substance for the definition of the unit of mass in the metric system of units. The *gramme* was intended by Borda to be the mass of 1 c.c. of water at 4° C., but the gramme in actual use is probably slightly smaller than this standard.

The general features of the expansion of water are exhibited in the following experiments :—

Experiment 24.—Fill a small expansion flask or dilatometer with water at 0° C. Place the dilatometer in a bath of water at 0° C., and place a thermometer in the bath to indicate its temperature.

Note the level of the water in the stem of the dilatometer at 0° C., and then heat the bath gently so as to raise its temperature slowly. Now follow the apparent expansion of the water in the dilatometer as the temperature rises from 0° C. to 80° C.

It will be found that the water at first contracts and, apparently, continues to contract at a gradually decreasing rate until a tempera-

ture of about 5° C. is reached. It then, apparently, begins to expand and continues to expand at a gradually increasing rate up to the boiling point.

This experiment shows that water contracts as the temperature rises from 0° C. to a temperature a little below 5° C., and then expands from this temperature up to the boiling point. The temperature at which it ceases to contract and begins to expand—that is, the temperature at which it attains its *maximum density*—is evidently *below* 5° C., for at this temperature it *appears*, in the glass dilatometer tube, to be neither expanding nor contracting, and must, therefore, be *really* expanding at the same rate as the glass of the tube.

Experiment 25.—Fill an expansion flask or dilatometer tube with water at the ordinary temperature. Place the bulb of the dilatometer in alcohol in a tall narrow beaker containing a thermometer. Now place the beaker in a freezing mixture so as to cool the alcohol bath in which the dilatometer has been placed to a temperature well below 0° C.

The water in the dilatometer can, in this way, be cooled below 0° C. without freezing. This, however, is not a peculiarity in the behaviour of water ; most liquids can, under similar conditions, be cooled below their freezing point without freezing.

It will be found that as the water in the dilatometer cools it contracts, and apparently continues to contract to about 5° C. as before ; it then begins to expand and continues to expand until it freezes at a temperature which may be as low as − 20° C., or even lower.

That is, water expands in cooling from its temperature of maximum density not only down to 0° C., but to any temperature below 0° C., at which it remains unfrozen.

It will be seen from these experiments that the volume of a given quantity of water changes with change of temperature in such a way as to pass through a minimum value at a temperature a little below 5° C., and that water, therefore, attains its *maximum density* at this temperature.

The determination of the exact value of the temperature of maximum density for water has been the subject of several important researches. A comparatively simple experiment devised by Hope for this purpose, and commonly known as **Hope's Experiment**, is of special interest.

A tall glass jar, shown in Fig. 35, is surrounded with a circular trough midway in its length, and is provided with two side tubes, one near the top and the other near the bottom, through which two thermometers may be fitted in a horizontal position as shown in the figure.

The jar is filled with water at the ordinary temperature, and a freezing mixture of ice and salt is placed in the circular trough.

If the readings of the two thermometers are now followed it will be found that at first the lower thermometer rapidly sinks until it reaches 4° C., while the upper one remains practically
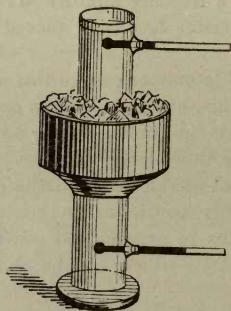
Fig. 35.

unchanged. After a time, however, the upper thermometer begins to fall, and ultimately falls to 0° C., while the lower one remains constant at 4° C. If the experiment lasts long enough a thin sheet of ice may form on the surface of the water, but the lower thermometer does not fall below 4° C.

The experiment indicates clearly that water attains its maximum density at 4° C. At first the water cooled by the freezing mixture in the trough contracts, and so, becoming denser than the water below it, sinks to the bottom, where it causes the fall of temperature indicated by the lower thermometer. This process goes on so long as water contracts on

cooling, and during the process the coldest and densest layers collect at the bottom of the jar. When, however, the temperature at which water attains its maximum density is passed, the water cooled by the freezing mixture expands on cooling, and becoming less dense than the water above it, rises to the surface, and causes the fall of temperature indicated by the upper thermometer. This process will evidently continue till all the water above the trough is reduced to 0° C. The temperature of the water below the trough will, however, vary from 0° C. at the level of the trough, to the temperature of maximum density at the bottom of the jar, where the coldest and densest layer is found. The temperature finally indicated by the lower thermometer during the progress of the experiment thus gives the temperature of the maximum density of water. This temperature is found to be almost exactly 4° C.

The real expansion of water is very conveniently studied by means of a **constant volume dilatometer**. An ordinary dilatometer containing a quantity of mercury, whose volume is about one-seventh the capacity of the tube, has practically the same capacity at all temperatures. The coefficient of expansion of mercury is about seven times the coefficient of cubical expansion of glass, so that when the volume of the mercury inside the dilatometer tube is one-seventh the capacity of the tube, the change in volume of the mercury for any change of temperature is practically the same as the corresponding change in the capacity of the tube. The space inside the tube unoccupied by the mercury is, therefore, of practically constant volume at all temperatures.

It will be evident on consideration that in order to construct an *accurate* constant volume dilatometer, it would be necessary to know the exact value of the coefficient of cubical expansion of the material of the tube. The constant volume dilatometer method of studying the real expansion of a liquid is, therefore, essentially the same as that described in Art. 28. In practice it

would be somewhat troublesome for *accurate* work, but for approximately accurate laboratory work it is an extremely convenient method.

> **Experiment 26.**—Take an expansion flask or a dilatometer with a large bulb, and convert it into a constant volume dilatometer by placing the proper quantity of mercury in the bulb. Then fill the dilatometer with water, and place it in a bath of ice and water. Provide the bath with a stirrer and a sensitive thermometer, and arrange to heat it very gently.
>
> Maintain the bath at 0° C. by means of ice for some time until the reading of water column in the dilatometer stem is steady. Note this reading. Then heat the bath gently so as to raise its temperature very slowly, and take the reading of the water column in the dilatometer stem for every degree rise of temperature up to 10° C. In taking these readings care must be taken to stir the water in the bath thoroughly before taking a reading.
>
> From the data thus obtained plot a curve showing the change in the height of the water column in the dilatometer as the temperature rises.
>
> This curve should be of the form shown in Fig. 36. It evidently indicates how the volume of the water in the dilatometer changes for each degree rise of temperature, and shows that water attains its maximum density at 4° C.

The fact that water attains its maximum density at a temperature higher than its freezing point is of great importance in the economy of nature. The water in lakes and ponds becomes cooled at the surface, and the surface layer sinks. As in Hope's experiment, however, the temperature at the bottom never falls below 4° C., and it is only at the surface that the temperature can fall to the freezing point. In still water, therefore, ice forms at the surface, and the temperature of the water below it ranges from 4° C. at the bottom to 0° C. at the top, just under the ice.

In this way plant and animal life in ponds and rivers is preserved from destruction during frosty weather.

If water reached its maximum density at 0° C., and if, at the same time, it contracted instead of expanding on freezing, ice

would form and remain at the bottom, and water would freeze from the bottom upwards into a solid mass of ice.

The following table gives the density of water and the volume of 1 gramme of water at temperatures between 0° C. and 100° C.,
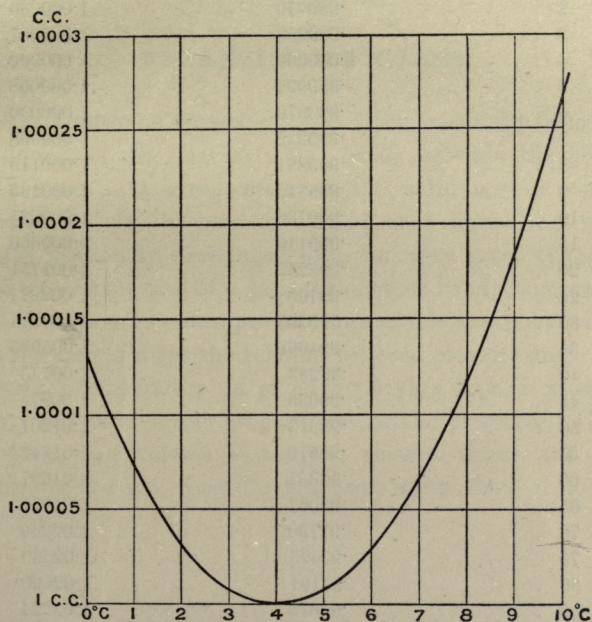

Fig. 36.

on the assumption that a cubic centimetre of water at 4° C. weighs exactly one gramme. It will be seen from this table that the mean coefficient of real expansion of water for a given range of temperature varies very considerably with the range for which the mean is taken.

Table giving the Density of Water and the Volume of one Gramme of Water at Temperatures from 0° C. to 100° C.

Temperature.	Density.	Volume.
0° C.	·999874	1·000127
1	·999930	1·000071
2	·999970	1·000030
3	·999993	1·000007
4	1·000000	1·000000
5	·999992	1·000008
6	·999970	1·000030
7	·999932	1·000068
8	·999881	1·000119
9	·999815	1·000185
10	·999736	1·000265
15	·999146	1·000850
20	·998252	1·001751
25	·997098	1·002911
30	·995705	1·004314
35	·994098	1·005936
40	·99233	1·00733
45	·99035	1·00974
50	·98813	1·01201
55	·98579	1·01442
60	·98331	1·01697
65	·98067	1·01971
70	·97790	1·02260
75	·97495	1·02569
80	·97191	1·02890
85	·96876	1·03224
90	·96550	1·03574
95	·96212	1·03938
100	·95863	1·04315

The density of pure water free from dissolved air at 4° C. is probably about ·99996 gramme per cubic centimetre.

CHAPTER V.

EXPANSION OF GASES.

29. Expansion of Gases. — Gases differ essentially from solids and liquids in the relation which exists between the pressure and volume of a given mass of the substance at constant temperature. In the case of a solid or a liquid the volume remains practically unchanged even for very great changes in pressure. In the case of a gas, on the other hand, comparatively small changes of pressure produce appreciable changes in volume.

In the case of a gas the relation between pressure and volume at constant temperature, as given by **Boyle's Law,** is such that the volume is inversely proportional to the pressure. That is, if v denote the volume of a given mass of a gas, and p the pressure of the gas, then Boyle's Law states that, at constant temperature,

$$v \propto \frac{1}{p},$$

or, $$pv = k,$$

where k is a constant.

Now, in studying the effect of change of temperature on a gas, it is necessary to enclose a quantity of the gas in a closed vessel, and the effect of change of temperature on the volume and pressure of the enclosed gas will obviously depend upon the nature of the constraint imposed upon the gas by the walls of the vessel.

Thus, when the air in the flask, shown in Fig. 3, is heated, as in Exp. 3, its volume increases, for it displaces liquid from the flask into the vertical tube; its pressure also increases, for

the liquid is forced into the tube against a gradually increasing pressure, due to the rise of the column of liquid in the tube.

If, however, the gas is enclosed in the bulb of a dilatometer tube by a short thread of mercury in the stem, as shown in Fig. 37, the effect of a change of temperature will be to produce a change of volume without a change of pressure; that is, the gas expands or contracts under *constant pressure*. The pressure in this case cannot change so long as the atmospheric pressure external to the mercury index in the stem remains constant. If the tube is fixed in a horizontal position the gas expands and contracts at a constant pressure, equal to the external atmospheric pressure.

A different case presents itself if we suppose the gas to be enclosed in a sealed glass vessel. The gas in this case cannot change in volume with change of temperature; its pressure will, however, change as the temperature changes, increasing with rise of temperature, and decreasing with fall of temperature. In this case the effect of change of temperature is to produce change of pressure without change of volume — that is, change of pressure at *constant volume.*
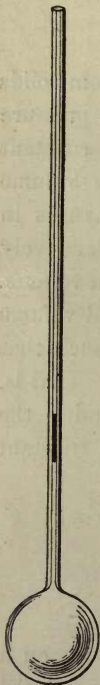
It will now be understood that if a given mass of gas be heated in a closed vessel, and shows an increase in volume, and also in pressure, the observed increase in volume really represents the increase due to the rise of temperature diminished by the decrease caused by the attendant increase in pressure. It is evident, therefore, that in order to study the real effect of change of temperature on the volume or on the pressure of a given mass of gas, it is necessary to separate the two effects, and to investigate, in the one case, change of volume at constant pressure, and in the other case, change of pressure at constant volume.

Fig. 37.

30. Expansion of a Gas under Constant Pressure.—

Change of volume with change of temperature at constant pressure, is the general case of expansion, as already considered in dealing with solids and liquids.

The expansion of a gas at constant pressure may be studied conveniently by the method of the experiment described below.

Experiment 27.—Take a length of about half a metre of uniform thick-walled capillary tubing of not more than 1 mm. bore. Fill about half the length of the tube with *dry* air, separated from the external air by a thread of mercury about 3 cm. in length. This may be done satisfactorily in the following way :—

Draw out the tube near one end to a narrow neck, as shown at A in Fig. 38, and bend a short piece about 2 cm. long at the other end at right angles, as shown at B in the figure.
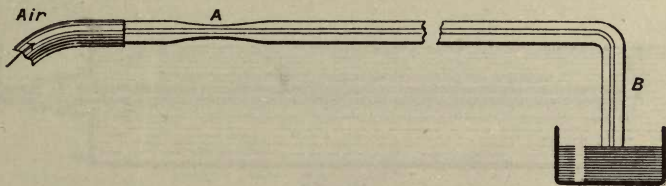
Fig. 38.

Support the tube horizontally with the end at B under mercury, and pass a current of well dried air through the tube from the other end. While the current of air passes through the tube heat it carefully with a Bunsen flame so as to remove all traces of moisture from the inner wall of the tube. When this drying process has lasted for some time seal off the tube at A, and allow it to cool with the end at B still under the mercury. It will be found that as the tube cools a thread of mercury is forced into the tube. Take the end of the tube out of the mercury when the thread is long enough, and set the tube aside with the bent end at B pointing upwards, ready for use.

The tube can evidently be filled with any gas by this method. When the tube has been dried by air, a stream of the dry gas is passed through for some minutes, and the tube then sealed.

Now take a long metal trough, as shown at CD in Fig. 39, and fit the tube AB with a rubber stopper into the tubulure provided at one end of the trough. Then attach a thermometer and a scale

to the tube with small rubber bands in the manner shown in the figure.

The scale is best etched on the tube itself, but a glass rod or tube, or a strip of porcelain, divided into any small equal divisions, serves as well.

The apparatus is now ready for use. First fill the trough with melting ice, and when the reading is steady read the length of the air column in the tube on the scale provided for this purpose. This length may be taken as a measure of the volume of the air in the tube. Now pour water into the trough and apply heat until the ice all melts, and the temperature begins to rise. As the temperature rises take the reading of the length of the air column every 10°, taking care to stir the water thoroughly before taking a reading. The tube should also be tapped before a reading is taken, for the mercury thread is liable to stick in the tube.

Continue this up to 100° C. if the tube is long enough for readings to be taken up to that temperature.
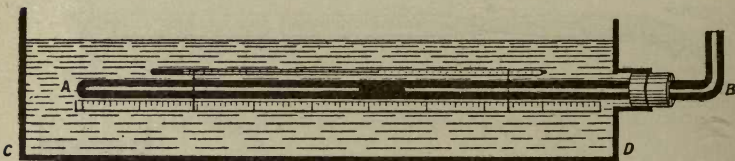
Fig. 39.

From the data thus obtained calculate the mean coefficient of expansion of the air between 0° C. and each temperature at which a reading was taken.

It will be found, if the experiment has been carefully performed, that the mean coefficients of expansion thus obtained are all practically equal. This shows (as far as the accuracy of the experiment goes) that the air expands quite uniformly with rise of temperature, as indicated by a mercury-in-glass thermometer. It will also be noted that the value of the coefficient is much greater than the values obtained in the case of solids or liquids. It is, for example, more than twenty times the coefficient of expansion of mercury.

The coefficient given by this experiment is, of course, the coefficient of *apparent* expansion of air in glass. The value of the coefficient is, however, so much greater than the coefficient of cubical expansion of glass that an approximate value of the latter may be used in making the necessary correction.

Numerical Example.—In an experiment of this kind the following readings were obtained of the length of the air column :—

		mm.
Length at	0° C.	= 303.
,,	10° C.	= 314.
,,	20° C.	= 326.
,,	30° C.	= 337.
,,	40° C.	= 348.
,,	50° C.	= 359.
,,	60° C.	= 370.
,,	70° C.	= 381.
,,	80° C.	= 392.
,,	90° C.	= 403.
,,	100° C.	= 414.

From these readings it will be seen that the mean coefficient of expansion of air works out to practically the same value for any range we choose to take. Thus, the mean coefficient between 0° C. and 50° C. is given by

$$\frac{359 - 303}{303 \times 50} = \frac{56}{303 \times 50} = \cdot 00369,$$

and the mean coefficient between 0° C. and 100° C. by

$$\frac{414 - 303}{303 \times 100} = \frac{111}{303 \times 100} = \cdot 00366.$$

The mean coefficient of *apparent* expansion of air in glass between 0° C. and 100° C. is thus given by this experiment to be ·00366. Hence, in the relation $c = a + g$, we have $a = \cdot 00366$, and if g be taken as ·000026 we get $c = \cdot 003686$.

It should be noticed, however, that the two values of a given by the experiment differ by 3 in the third significant figure. This indicates that the experiment is not accurate enough to give a reliable value for the third significant figure in the result, and that in this case it is practically useless to apply a correction for the expansion of the glass. This correction would be of importance only in an experiment in which, at least, the third significant figure is reliable.

Another point to be noted in connection with this calculation is that the value of the coefficient of expansion is too great to admit of the use of any of the approximations which may be used with the smaller coefficients for liquids and solids.

Thus the mean coefficient of expansion of air between 10° C. and 100° C. cannot be taken as $\frac{414 - 314}{314 \times 90}$ without serious error.

It must be taken as $\dfrac{414 - 314}{303 \times 90}$, that is, the initial volume must be taken at $0°\ C$.

The experiment described above shows that, as far as the accuracy of the experiment goes, air expands uniformly with rise of temperature, as indicated by a mercury-in-glass thermometer, and that its coefficient of expansion, found to be about ·0036, is much greater than the coefficients of expansions for liquids and solids.

If now the experiment be repeated for a number of different gases, it will be found that not only will the same general results be obtained in each case, but the coefficient of expansion will be found to have the same value for each gas.

This result is so important that it has been the subject of much careful experimental research, and it is found to be a general law that all gases which obey Boyle's Law expand equally with change of temperature, and have the same coefficient of expansion.

This law, known as **Charles' Law** in England and as **Gay Lussac's Law** in France, states that the coefficient of expansion at constant pressure is the same for all gases which obey Boyle's Law, and that for any gas the mean coefficient of expansion at constant pressure for any range of temperature within which Boyle's Law holds for that gas, is ·003665, or about $\frac{1}{273}$.

That is, for any gas which obeys Boyle's Law, the volume at constant pressure changes by $\frac{1}{273}$ of its volume at $0°$ C. for each degree Centigrade change of temperature.

The experimental determination of the exact value of the coefficient of expansion of a gas at constant pressure is a matter of some difficulty. The method described in Exp. 27 above, is simple and convenient, but it does not give accurate results. A more accurate determination of the mean value of the coefficient between $0°$ C. and $100°$ C., may be made by the method of the experiment described below.

Experiment 28.—Fit up the apparatus shown diagrammatically in Fig. 40. The tubes AB and CD are straight pieces of glass tubing about 6 mm. in bore joined to a T piece, BCE, at B and C, and fitted in the manner shown in the figure into a wide glass tube, KL. The T piece is joined at E by a length of thick-walled rubber tubing to a short length of fairly wide tube, intended to serve as a reservoir for mercury.

The tube AB is carefully dried and filled with pure dry air as described above. It is then connected, while partly filled with mercury, with the tubes CD and EFG, and mercury is poured into the system of tubes until it stands about half way up AB when the level is about the same in the three tubes.

It will be seen from a consideration of this arrangement that the pressure of the air in the tube AB can at any temperature be adjusted to exact equality with the atmospheric pressure. The tube CD communicates with the atmosphere at D, and the column of mercury in it is always in hydrostatic equilibrium with the column in AB. It follows, therefore, that if the mercury columns in the tubes AB and CD are adjusted to the same level by raising or lowering the tube FG, the pressure of the air in AB will be exactly equal to the atmospheric pressure.

The tube AB may, conveniently, be graduated like a burette or eudiometer tube, so that the volume of the air in it may be read off directly on the scale when required ; or the volume of the air may be taken as proportional to the length of the tube which it occupies, and this length can be observed on a mm. scale engraved on the tube or attached to it in any convenient way.

The wide tube KL is fitted with an inlet and exit tube, so that a current of steam or water at any required temperature may be passed through it. A thermometer may be fixed inside the tube to give the temperature.

Fig. 40.

In fitting up this apparatus it is very important, even for a labora-

tory experiment, to make quite sure that the air and mercury in the tube AB are perfectly dry.

When the apparatus is ready for use a determination of the mean coefficient of expansion of air in constant volume is readily made. Fill the tube KL with small pieces of melting ice and water, or pass a current of ice-cold water through it, adjust the columns of mercury in the tubes AB and CD to the same level, and record the volume of the air in AB. Let this volume be denoted by V_o.

Then pass a current of steam through the tube, adjust the level of the mercury as before, and again record the volume of the air in the tube. Let this volume be denoted by V_{100}.

From these data the mean coefficient of expansion of air at constant pressure between 0° C. and 100° C. is at once given by

$$c = \frac{V_{100} - V_o}{100\ V_o}.$$

Numerical Example.—In an experiment of this kind the values obtained for V_o and V_{100} were—

$$V_o = 25 \cdot 1 \text{ c.c.}$$
$$V_{100} = 34 \cdot 3 \text{ c.c.}$$

This gives

$$c = \frac{34 \cdot 3 - 25 \cdot 1}{25 \cdot 1 \times 100} = \frac{9 \cdot 2}{2510} = \cdot 00366.$$

That is, the mean coefficient of expansion of air at constant pressure, between 0° C. and 100° C., is found to be ·00366, or, almost exactly, $\frac{1}{273}$.

Accurate experiments show that the coefficient of expansion at constant pressure is not *exactly* the same for all gases which conform to Boyle's Law. Just as different gases which "obey Boyle's Law" in the accepted sense, deviate to different extents from *strict* conformity to the law, so they show slight differences in the value of the coefficient of expansion. Thus Regnault found the following values of the coefficient for air, hydrogen, and carbon dioxide at a constant pressure of one atmosphere :—

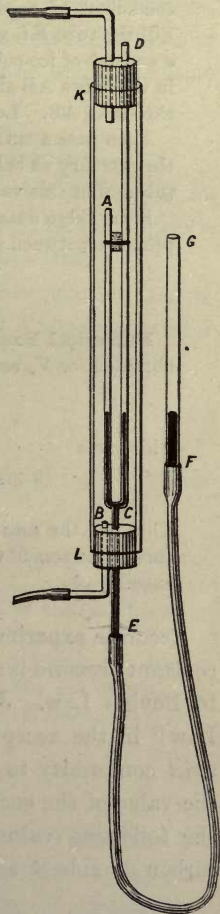|	
Air, ...	·003671
Hydrogen, ...	·003661
Carbon dioxide, . . .	·003710

It is found, too, as the result of experiment that, although the

value of the coefficient of expansion at constant pressure is practically the same at all pressures, it varies slightly with the pressure in a manner which depends upon the nature of the gas.

It follows from Charles' Law that if V_o denote the volume of a given mass of a gas at 0°C., and V_t its volume under the same pressure at $t°$ C., then,

$$V_t = V_o (1 + ct),$$

where c denotes the mean coefficient of expansion of the gas at constant pressure between 0° C. and $t°$ C., and has the approximate value $\frac{1}{273}$ for all gases which obey Boyle's Law.

It is to be noted, too, in connection with this relation that if $V_{t'}$ denote the volume of the gas at $t'°$ C., and V_t its volume at a higher temperature, $t°$ C., then

$$c = \frac{V_t - V_{t'}}{V_o (t - t')},$$

and that c is too great for $V_{t'}$, to be substituted for V_o in this relation without considerable error.

Numerical Example.—The volume of a given mass of gas under constant pressure is found to be 147 units at 20° C., and 187 units at 100° C., find the mean coefficient of expansion of the gas between 20° C. and 100° C.

Here the expansion of the gas is at the rate of $\frac{1}{2}$ unit per degree Centigrade rise of temperature ; the volume of the gas at 0° C. is, therefore, given by $V_o = (147 - 20 × \frac{1}{2})$ units = 137 units. Hence —

$$c = \frac{187 - 147}{137 × 80} = \frac{40}{137 × 80} = \frac{1}{274}.$$

31. **Increase of Pressure at Constant Volume.**—It has already been noted that when a given quantity of any gas undergoes change of temperature without change of volume, the pressure of the gas changes, and is found to increase as the temperature rises, and to decrease as the temperature falls.

It is, therefore, of interest to determine the relation between the pressure and temperature of a gas while the volume remains

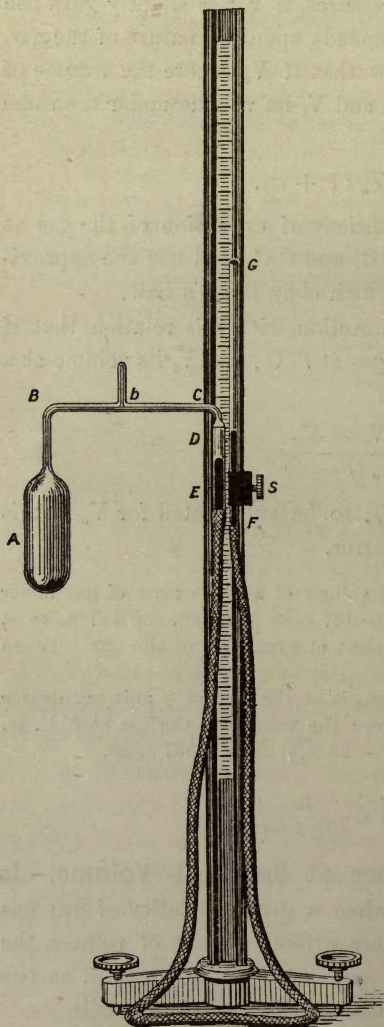constant. This relation may be studied by the method of the following experiment.

Fig. 41.

Experiment 29.—Set up the apparatus shown in Fig. 41. The bulb and stem ABCD is practically a dilatometer with a comparatively large bulb and a stem of fine bore bent twice at right angles as shown at B and C. At D the stem opens into a wider tube, DE, which is joined by a length of thick-walled rubber tubing, EF, to the tube FG, which should be of the same bore as DE. The tubes DE and FG are mounted on a wooden stand in the manner shown in the figure. The tube DE is fixed to the stand in such a way as to allow the bulb and stem of the dilatometer tube to project beyond the edge of the stand. The tube FG is carried by a slide S, so that it can be moved up and down the stand and fixed at any point by means of the screw with which it is provided. The bulb and stem of the tube ABCD are filled with *dry* air. This is done, once for all, by connecting the tube to an air pump through a range of drying tubes, and then alternately exhausting it and allowing it to fill with air through the drying tubes, until the inner wall is quite free from moisture, and the tube is filled with perfectly dry pure air. The connection to the air pump is most conveniently made through a small side tube, *b*, which can be sealed off when the tube is filled.

The tubes DE and FG, and the rubber tubing EF which connects them, are filled with pure *dry* mercury, and serve as a manometer tube for adjusting and measuring the pressure of the air in the bulb. A millimetre scale mounted on the stand is provided to measure the difference in the level of the mercury in the two limbs of the manometer tube.

In order to maintain the air in the bulb at constant volume when it is subjected to change of temperature, a mark is engraved on the tube DE at D, just below the point where the narrow bore of the stem opens out into the wider bore of DE, and the mercury in DE is adjusted to this mark whenever the pressure exerted by the air at any temperature is measured.

When the apparatus is set up ready for use surround the bulb A with small pieces of melted ice in a beaker so as to reduce the temperature of the air in the bulb to 0° C. Then adjust the position of the tube FG on the stand until the mercury in DE stands at the constant volume mark, and read off the difference in the level of the mercury in the two tubes. Let this difference be h_0 mm.

Now add some water to the ice in the beaker, and heat the water, so that the temperature rises slowly. As the temperature rises read the difference in the level of the mercury in the two limbs of the manometer tube every 10°, the air being adjusted to constant volume at each reading, and the bath stirred thoroughly before a reading is taken. Let h_t mm. be the observed difference in level at any temperature $t°$ C.

Then, if H denote the height of the barometer in mm. at the time of the experiment, the pressure of the air at 0° C. is that due to $(H + h_0)$ mm. of mercury, and at $t°$ C. in the same way the pressure is that due to $(H + h_t)$ mm. of mercury. For strict accuracy these heights should be reduced to the equivalent heights at 0° C.

It will be found on studying the results obtained that the increase in pressure of the air at constant volume for each 10° rise of temperature is practically the same. For example, in an experiment of this kind the following results were obtained :—

Rise of temperature.	Increase of pressure as indicated by the increase in the difference in the level of the mercury in the two limbs of the manometer tube.	
0° C. to 10° C.,	. . . . . .	28·0 mm.
0° C. to 20° C.,	. . . . . .	55·8 ,,
0° C. to 30° C.,	. . . . . .	83·9 ,,
0° C. to 40° C.,	. . . . . .	111·8 ,,
0° C. to 50° C.,	. . . . . .	140·0 ,,
0° C. to 60° C.,	. . . . . .	168·0 ,,
0° C. to 70° C.,	. . . . . .	195·9 ,,
0° C. to 80° C.,	. . . . . .	224·1 ,,
0° C. to 90° C.,	. . . . . .	251·9 ,,
0° C. to 100° C.,	. . . . . .	279·9 ,,

That is, the pressure of the air at constant volume changes uniformly with change of temperature, as indicated by a mercury-in-glass thermometer.

It should be noted that in this experiment the volume of the gas is only *apparently* constant. It increases with the increase in the capacity of the bulb as the temperature rises. A small error is also introduced by the fact that the air in the stem of the tube is not heated to the same temperature as the air in the bulb.

This experiment shows (as far as its accuracy goes) that, in the case of air, the pressure at constant volume increases with rise of temperature on the mercury-in-glass scale at a definite constant rate.

When this experiment is tried with other gases it is found that exactly the same result is obtained for all gases which obey Boyle's Law. The pressure at constant volume is found to increase with the temperature at a uniform constant rate in each case, and *if this rate is expressed as a fraction of the initial pressure at 0° C. it is found to be the same for all gases*. It is, therefore, possible and convenient to express this rate of increase of pressure of a gas at constant volume as a coefficient analogous to the coefficient of increase of volume at constant pressure, or the coefficient of expansion of the gas.

The **mean coefficient of increase of pressure of a gas at constant volume** for any given range of temperature may, therefore, be defined as the ratio of the average increase of pressure per degree centigrade for the given range to the initial pressure of the gas at 0° C.

Numerical Example.—In the experiment described above, the height of the barometer was found to be 758 mm.

The values of h_0 and h_{100} were also recorded as :—

$h_0 = 2 \cdot 4$ mm.   (Higher in tube FG than in DE.)

$h_{100} = 282 \cdot 3$ mm.

It follows from this that the pressure of the gas at 0° C., P_0, is given in mm. of mercury by :—

$$P_0 = (758 + 2 \cdot 4) \text{ mm.,}$$

or, $P_0 = 760 \cdot 4$ mm.

The mean coefficient of increase of pressure at constant volume, between 0° C. and $t°$ C., is, therefore, given by

$$c = \frac{282 \cdot 3 - 2 \cdot 4}{760 \cdot 4 \times 100} = \frac{279 \cdot 9}{760 \cdot 4 \times 100},$$

or, $\qquad c = \cdot 00367.$

That is, the mean coefficient of increase of pressure at constant volume between 0° C. and 100° C. for air has a value $\cdot 00367$, or about $\frac{1}{273}$, which is exactly the same as the value found for the coefficient of expansion or the coefficient of increase of volume at constant pressure.

The result thus obtained for air is found to be generally true. In the case of all gases which obey Boyle's Law, the coefficient of increase of pressure at constant volume is practically the same as the coefficient of increase of volume at constant pressure. That is, the pressure of a given mass of gas at constant volume increases by $\frac{1}{273}$ of its pressure at 0° C. for each degree centigrade change of temperature for the range within which the gas obeys Boyle's Law.

The law of the increase of pressure at constant volume is, therefore, the same for all gases which obey Boyle's Law, and may be stated by saying that the coefficient of increase of pressure of a gas at constant volume has an approximate value $\frac{1}{273}$, and is, therefore, approximately equal to the coefficient of increase of volume at constant pressure.

That is, if P_o denote the pressure of a given mass of gas at 0° C., and P_t its pressure at $t°$ C. at the same volume, then $P_t = P_o (1 + ct)$, where c is the mean coefficient of increase of pressure at constant volume between 0° C. and $t°$ C., and has the approximate value, $\frac{1}{273}$, for all gases which obey Boyle's Law.

This law is not independent of Boyle's and Charles' Laws; it is involved in these laws, and can be deduced from them theoretically.

The exact value of the coefficient of increase of pressure at constant volume for different gases has been the subject of much

research. Regnault found the mean value of the coefficient for air between 0° C. and 100° C. to be ·0036679, but the general result of his work and of other researches goes to show that the value of the coefficient differs slightly for different gases, and is not exactly the same as the coefficient of increase of volume at constant pressure for any gas. It has been found, too, that the coefficient increases slightly as the value of the initial pressure at 0° C. increases.

32. The Gas Thermometer.—It will be clear from what has been said on the expansion of gases, that a gas which obeys Boyle's Law is, in many ways, specially suitable for use in an expansion thermometer as the standard thermometric substance.

The coefficient of expansion of a gas is great, so that not only would a gas thermometer be very sensitive to changes of temperature, but its readings would be practically independent of variations in the expansibility of the material of the tube.

The wide limits of temperature within which a properly selected gas may be used for thermometric purposes, is another advantage of the gas thermometer over any liquid-in-glass thermometer. Thus air, hydrogen, nitrogen, and other gases obey Boyle's Law through a very wide range of temperature, and may be used for the measurement of temperature from the highest attainable temperature down to very low temperatures.

A gas-expansion thermometer may be based on the expansion of a gas at *constant pressure,* or the increase in pressure of a gas at *constant volume.* The apparatus shown in Fig. 40 would serve as a *constant-pressure gas thermometer,* while the apparatus shown in Fig. 41 is the usual form of a *constant-volume gas thermometer.*

It will be recognised at once that the form of apparatus necessary for a constant-pressure air thermometer is not adapted for general use as a thermometer. The expansion of the gas at constant pressure is, for any considerable rise of temperature, so great that a large proportion of the gas must be in the stem of the thermometer tube, and as it is generally difficult to expose

more than the bulb of the thermometer to the temperature to be measured, the correction for the temperature of the air in the stem, therefore, becomes troublesome and uncertain.

The constant-volume gas thermometer is not open to this objection. The gas is confined, practically, to the bulb at all temperatures, and in order to determine any temperature it is only necessary to measure the pressure of the gas at the required temperature.

The constant-volume thermometer is, therefore, the type of gas thermometer which has generally been used. The apparatus shown in Fig. 41 is a convenient form of the constant-volume *air thermometer* devised by Professor Joly of Dublin.

The theory of the constant-volume gas thermometer is comparatively simple. Let P_t denote the pressure of the gas in the bulb at any unknown temperature, t° C., and let P_o denote the pressure of the gas at 0° C.; then, since

$$c = \frac{P_t - P_o}{P_o t},$$

it follows that

$$t = \frac{P_t - P_o}{P_o c}.$$

Of the quantities P_t, P_o, and c, which thus determine t, P_t is found by experiment, P_o must be determined, once for all, for the thermometer, and c, the coefficient of increase of pressure at constant volume, is a known constant.

The value of t can, therefore, be determined with a given thermometer by simply measuring P_t, the pressure of the gas in the thermometer at the required temperature, t° C.

The great disadvantages of the gas thermometer for general use arise out of the fact that it is, necessarily, a somewhat large and cumbersome piece of apparatus, and that it is necessary to make a careful and exact measurement of pressure at each determination of temperature. The instrument cannot conveniently be provided with a scale of temperature for direct

reading, for the pressure at any temperature involves the height of the barometer, and this height is variable.

The gas thermometer is, therefore, never used for the measurement of temperature in the ordinary way. It is, however, generally adopted as a **standard thermometer**. In all accurate experimental work, temperatures are specified on some recognised form of gas thermometer, usually the **air thermometer**, the **hydrogen thermometer**, or the **nitrogen thermometer**. Determinations of temperature on the gas-thermometer scale are not, however, always made directly with a gas thermometer; it is generally more convenient to use a mercury-in-glass thermometer which has been standardised by direct comparison with a standard gas thermometer.

It has been stated above that the temperature corresponding to a pressure P_t of the gas in the constant-volume gas thermometer is given by

$$t = \frac{P_t - P_o}{P_o c}.$$

Now, the lowest value which P_t can conceivably have is zero, so that assuming the relation here given to hold at all temperatures the lowest temperature to which the gas can conceivably be reduced, is given by

$$t = \frac{0 - P_o}{P_o c} = -\frac{1}{c};$$

or, taking the value of c as $\frac{1}{273}$,

$$t = -273.$$

The temperature $-273°$ C. is thus the lowest conceivable temperature on the scale of the gas thermometer, if we assume the properties of the gas to remain unchanged by fall of temperature.

This result is obvious without the use of the formula. For, since the pressure of a gas at constant volume decreases by $\frac{1}{273}$ of its value at $0°$ C. for each degree fall of temperature, it

is evident that at − 273° C. the pressure must be zero, for it will have been reduced by $\frac{273}{273}$ of its value at 0° C. if we suppose the properties of the gas unchanged by the fall of temperature.

This temperature of − 273° C. is commonly known as **the absolute zero** of the gas thermometer.

It will be seen that if temperatures on the Centigrade scale are measured from this absolute zero as the zero of the scale, the melting point of ice (0° C.) becomes 273 on this scale, and the boiling point of water (100° C.) becomes 373 on the scale. Temperatures measured in this way from the absolute zero of the gas-thermometer scale are called **absolute temperatures,** and it will be clear that the absolute temperature T, corresponding to any given temperature, $t°$ C., is given by the relation,

$$T = (273 + t).$$

This conception of an absolute scale of temperature is, for reasons which we cannot here consider, a very important one. It is introduced at this point because it is possible by its use to express the laws relating to the expansion of a gas in a very simple form.

It will be seen that on this scale a degree of temperature is $\frac{1}{273}$ of the absolute temperature at 0° C. (273 A.T.), and that, therefore, the volume of a gas at constant pressure, and the pressure at constant volume, both change with temperature in exactly the same way as the measure of the temperature on the absolute scale changes.

That is, the volume of a given mass of gas at constant pressure is directly proportional to the absolute temperature of the gas. This is a concise statement of Charles' Law.

Similarly, it may be stated that the pressure of a given mass of gas at constant volume is directly proportional to the absolute temperature of the gas.

7

Numerical Examples.—The following examples illustrate the use of absolute temperatures in calculations.

1. The volume of a given mass of gas under constant pressure is 23·4 c.c. at 10° C., find its volume at 20° C.

The absolute temperatures corresponding to 10° C. and 20° C. are 283 A.T. and 293 A.T. respectively. Hence, if v denote the volume of the gas at 20° C. we have, by Charles' Law,

$$\frac{23\cdot4}{v} = \frac{283}{293},$$

or, $v = 24\cdot2$ c.c.

That is, the volume at 20° C. is 24·2 c.c.

2. The pressure of the air in a constant-volume air thermometer was found to be 768 mm at 10° C., find the temperature indicated by a pressure of 821 mm.

Here, if T denote the absolute temperature indicated by the thermometer, we have—

$$\frac{283}{T} = \frac{768}{821};$$

and, therefore, $T = 302\cdot5.$

That is, the temperature indicated by the thermometer is 29·5° C.

33. The General Relation between the Pressure, Volume, and Temperature of a given Mass of Gas.—

The state of given mass of any gas is completely defined by its pressure, volume, and temperature.

It is now possible to establish a simple general relation between these three quantities. If p denote the pressure, v the volume, and T the absolute temperature of unit mass of a gas, then, by Boyle's Law,

$$v \propto \frac{1}{p} \text{ when T is constant;}$$

and by Charles' Law,

$$v \propto T \text{ when } p \text{ is constant.}$$

Hence, by combining these two relations algebraically, we get

$$\propto \frac{T}{p}.$$

That is,
$$v = R\frac{T}{p};$$

or,
$$\frac{pv}{T} = R,$$

where R is a constant.

This, then, is the general relation between the pressure, volume, and temperature of a given mass of a gas. It implies that the product, *pv*, divided by T for a given mass of gas, is constant for all co-existent values of *p*, *v*, and T.

It evidently involves the law of increase of pressure at constant volume, for if *v* be constant, we have $p = \frac{R}{v}T$, where R/*v* is a constant. That is, $p \propto T$ when *v* is constant.

It must be understood that no actual gas conforms exactly to this relation at all temperatures. Every gas shows characteristic deviations from the laws involved in the relations. At temperatures far removed from its condensing point, the deviations are small, but at temperatures approaching the condensing point, the deviations generally become so great that the relation, in the form here given, ceases to hold.

Numerical Exampels.—The following examples illustrate the use of the relation $\frac{pv}{T} = R$ (*a constant*) in calculation.

1. The volume of a given mass of gas at 10° C. and 758 mm. pressure is 10·4 c.c., find its volume at 0° C. and 760 mm. pressure.

Here, since $\frac{pv}{T}$ is *constant*, it has the same value for all states of the gas, and, therefore, if *v* denote the required volume at 0° C. and 760 mm., we have—

$$\frac{758 \times 10\cdot4}{283} = \frac{760\,v}{273};$$

or,
$$v = 10.$$

That is, the volume of the gas at 0° C. and 760 mm. pressure is **10** c.c.

2. The volume of a given mass of gas at 20° C. and 762 mm. pressure is 102·1 c.c., at what temperature will its volume be exactly 100 c.c. under a pressure of 760 mm.

Here, as above, if T denote the required absolute temperatures, we have—

$$\frac{762 \times 102\cdot1}{293} = \frac{760 \times 100}{T};$$

or, $T = 286\cdot3.$

That is, the temperature at which the volume of the gas is exactly 100 c.c. at a pressure of 760 mm. is 286·3 A.T., or 13·3° C.

CHAPTER VI.

CALORIMETRY.

34. Quantity of Heat.—The idea of heat as a quantity which can be measured has already been referred to. When a body rises in temperature through any given range it gains a definite quantity of heat ; when it falls in temperature through the same range it loses the same quantity of heat.

When equal masses of the same substance undergo the same change of temperature they gain or lose the same quantity of heat; and when different masses of the same material undergo the same change of temperatures they gain or lose quantities of heat which are directly proportional to their masses.

These statements are evident on first principles, without recourse to experiment.

When, however, equal masses of different substances undergo the same change of temperature, they presumably gain or loss different quantities of heat, but it is necessary to resort to experiment to decide this question. Again, when a given mass of any substance changes state, from solid to liquid, or from liquid to vapour, it absorbs a definite quantity of heat, and when the change of state is reversed it gives out the same quantity of heat.

It is evident, therefore, that in the study of heat, means must be found for the measurement of quantity of heat.

The measurement of heat is known as **calorimetry.**

35. The Unit of Heat.—Heat, as a form of energy, can, under certain conditions, be measured in the usual mechanical units of energy, ergs, or foot-poundals.

It is necessary, however, in the experimental study of heat to adopt a unit of heat associated with change of temperature.

The quantity of heat which a given mass of a definite substance gains or loses when it undergoes a given change in temperature is definite and constant, and may, therefore, be taken as a unit for the measurement of quantity of heat.

The **unit of heat** generally adopted is defined on this basis. It is **the quantity of heat required to raise one gramme of pure water from 0° C. to 1° C.** This unit of heat is called the **calorie.** If the unit is defined in this way it is evident that n units of heat is the quantity of heat required to raise n grammes of water from 0° C. to 1° C., and not the quantity required to raise 1 gramme from 0° C. to $n°$ C., or through n degrees rise of temperature; it cannot be *assumed* that the quantity of heat required to raise 1 gramme of water through 1° of temperature is the same for all degrees as it is for the degree from 0° C. to 1° C.

It is found, however, by experiment, that the quantity of heat required to raise 1 gramme of water through 1° is very nearly the same wherever the degree be taken between 0° C. and 100° C. The *unit of heat* may, therefore, for all practical purposes, be taken as *the quantity of heat required to raise the temperature of one gramme of pure water through one degree Centigrade.*

When the unit of heat is defined in this way it is evident that the quantity of heat required to raise m grammes of water from $t'°$ C. to $t°$ C. is $m (t - t')$ units, whatever the values of t and t' may be.

> **Experiment 30.**—Place 100 grammes of water at about 20° C. in a thin glass beaker containing a sensitive thermometer reading to fifths or tenths of a degree, and set the beaker standing on a slice of cork inside a larger beaker. Then take 100 grammes of water, cooled to 0° C. by immersing the beaker containing it in melting ice, and mix it with the water in the first beaker after carefully reading the temperature indicated by the thermometer. Stir the "mixture

carefully with the thermometer, and note the final reading when the mixing is complete. If the temperature of the water in the first beaker is recorded as 19° C., it will be found that the final temperature, after adding the ice-cold water, is about 9·5° C. Further, if the experiment be repeated a number of times with the water in the first beaker at any temperature between 0° C. and 100° C., it will always be found that the final temperature, after mixing with the water at 0° C., is always about half the initial temperature.

This experiment shows that the quantity of heat which a gramme of water gains or loses for 1° change of temperature is the same wherever the degree be taken. For, if we assume this to be true, and calculate the final temperature from the initial conditions, we get a result which agrees with the experimental result. Thus, if $t'°$ C. denote the final temperature, then when the 100 grammes of water at 0° C. is mixed with the 100 grammes at $t°$ C., the latter loses heat in cooling from $t°$ C. to $t'°$ C., while the former gains heat in rising in temperature from 0° C. to $t'°$C., and if we assume that the exchange of heat takes place only between the two masses of water, and that there is no loss or gain of heat during the mixing, to or from the surroundings, we may assume that the heat lost by the one quantity of water is equal to the heat gained by the other quantity. Now, if we make the assumption stated above, the heat lost by the warm water is 100 $(t - t')$ units, and the heat gained by the cold water is 100 $(t' - 0)$ units, or 100 t' units, so that we may write

$$100 \ (t - t') = 100 \ t',$$

or, $$200 \ t' = 100 \ t,$$

or, $$t' = \frac{t}{2}.$$

The final temperature found by experiment agrees with this result for all values of t, and so justifies the assumption on which the calculation is based.

It may be noted here that the method of the experiment described above is an example of the thermometric *method of*

mixtures by which two quantities of the same substance, or of different substances, at different temperatures, are mixed so as to allow of the free transfer of heat from the hot substance to the cold substances until the same common temperature is reached.

The experiment may be performed in a more general manner by mixing m grammes of water at any convenient temperature, $t°$ C., with m' grammes at any other temperature, $t'°$ C., and noting the final temperature, $θ°$ C., when the mixing is complete. The result of the experiment can then be compared with the value of $θ$ given by the equation,

$$m \, (t - θ) = m' \, (θ - t').$$

It is extremely difficult, however, in actual practice to obtain accurate results in an experiment of this kind. The exchange of heat is evidently not confined to the two quantities of water; the beaker and the thermometer necessarily take part in it. There is also some difficulty in determining the temperatures of the two masses of water at the instant of mixing, and it is impossible during the mixing to avoid loss or gain of heat by cooling or heating, according as the temperature of the mixture is above or below the temperature of its surroundings.

These difficulties can, however, be overcome by taking proper precautions, and it is found as the result of careful investigation that the unit of heat may, for general purposes, where very high accuracy is not essential, be taken as the quantity of heat necessary to raise one gramme of pure water through one Centigrade degree.

36. **The Water Calorimeter.**—The water calorimeter is a piece of apparatus designed for the measurement of heat in terms of the unit defined in the foregoing article by the method of mixtures.

It consists, essentially, of a vessel for holding the water, and a thermometer for measuring the change in the temperature of the water.

The vessel is cylindrical in form, about 8 cms. or 10 cms. high, and 5 cms. or 6 cms. in diameter, and is usually made of very thin spun copper, aluminium, or silver. It is mounted inside a larger vessel, which serves as a shield, either by suspend-
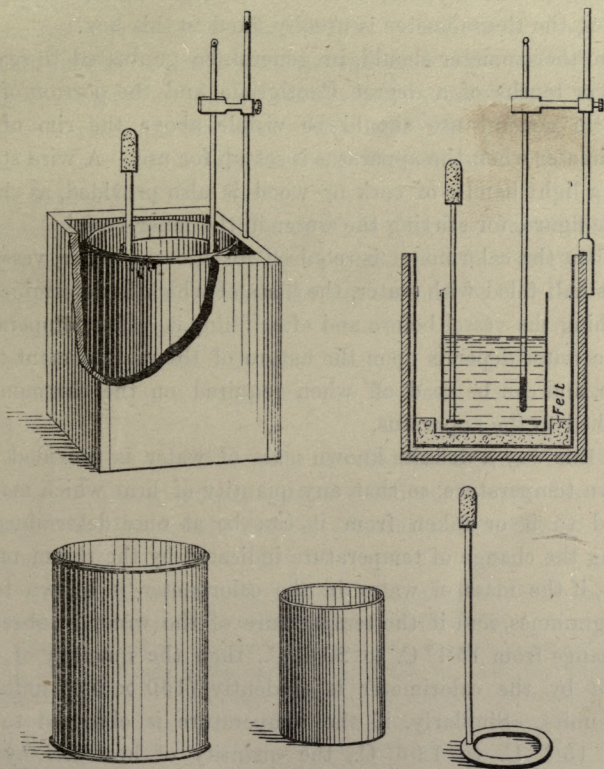

Fig. 42.

ing it with thread from the rim of the vessel, or by letting it rest on felt or on the points of conical cork supports fixed inside the outer vessel. It is thus protected from loss of heat by conduction to the outer vessel, and in order to diminish as

far as possible the loss of heat by radiation, the outer surface of the inner vessel and the inner surface of the outer vessel are both brightly polished or plated. It is generally convenient to fit the calorimeter and the outer vessel which protects it into a rectangular wooden box, as shown in Fig. 42, and a clip for holding the thermometer is usually fixed to this box.

The thermometer should, in general, be graduated to read to fifths or tenths of a degree Centigrade, and the portion of the scale in general use should be visible above the rim of the calorimeter when the apparatus is set up for use. A wire stirrer with a light handle of cork or wood is also provided, as shown in the figure, for stirring the water in the inner vessel.

When the calorimeter is required for use the inner vessel is about half filled with water, the mass of which is determined by weighing the vessel before and after filling it. The temperature of the water depends upon the nature of the measurement to be made, and can be read off when required on the thermometer attached to the apparatus.

In this way a definite known mass of water is provided at a known temperature, so that any quantity of heat which may be added to it or taken from it can be at once determined by noting the change of temperature indicated by the thermometer. Thus, if the mass of water in the calorimeter is known to be 150 grammes, and if the temperature of the water is observed to change from 15·1° C. to 20·6° C., then the quantity of heat *gained* by the calorimeter is evidently (150 × 5·5) units, or 825 units. Similarly, if the temperature is observed to fall from 15·1° C. to 12·6° C., the quantity of heat *lost* by the calorimeter is (150 × 2·5) units, or 375 units.

It will be seen from what has been said that the thermometer is of paramount importance in this apparatus. It is desirable, therefore, that the thermometer provided should be a sensitive instrument with an open scale reading accurately to fifths or tenths of a degree at least.

37. The Method of Mixtures.—The general nature of the method of mixtures has already been explained. The method, first introduced by Black, was adopted by Regnault in a number of important researches, and is now the calorimetric method in most general use.

The water calorimeter described in the foregoing Article is the instrument used in making measurements by this method. The body whose gain or loss of heat is to be measured is " mixed " with the water in the calorimeter, and the quantity of heat gained or lost by the calorimeter is determined in the manner explained above.

It must be understood that the term " mixing " in this relation merely means that the body is placed in free thermal communication with the water in any manner which admits of the direct exchange of heat essential to the method. It is not necessary, and, in most cases, it is impossible to mix the body with the water in the ordinary meaning of the word.

The following experiment for the determination of the average quantity of heat given out by one gramme of copper in cooling through one Centigrade degree, illustrates the practice of the method :—

Experiment 31.—Set up a water calorimeter ready for use. Let the mass of water in the calorimeter be 150 grammes.

Take a piece of copper wire at least 100 grammes in weight, roll it up into a loosely coiled mass and weigh it. Let the weight be 124·3 grammes. Now heat the mass of copper wire to 100° C. by suspending it by a silk fibre in boiling water, or in steam from boiling water, or better, in an oven or small enclosure heated by steam. While the copper is heating stir the water in the calorimeter, and note the temperature indicated by the thermometer. Let the temperature be 14·6° C.

Now remove the copper from the hot water or steam by means of the fibre, and transfer it at once as quickly as possible to the water in the calorimeter. Stir the water thoroughly during the "mixing" of the copper and the water, and note the final temperature of the water when the process is complete. Let this temperature be 21·1° C.

From these data the average quantity of heat lost by 1 gramme of copper in cooling through 1° C. can be easily calculated.

The heat gained by the water in the calorimeter is, evidently,

150 (21·1 − 14·6) units, or 150 × 6·5 units.

This, therefore, is the quantity of heat lost by 124·3 grammes of copper in cooling from 100° C. to 21·1° C., through 78·9° C. The average quantity of heat lost by 1 gramme of copper in cooling through 1° C. is therefore given by

$$\frac{150 \times 6\cdot5}{124\cdot3 \times 78\cdot9} \text{ unit, or } \cdot0994 \text{ unit.}$$

That is, as far as the accuracy of the experiment goes, the required quantity of heat may be taken as ·1 unit.

It should be noticed, however, that there are several important sources of error in this experiment. The error caused by the cooling of the hot copper during its transfer from the steam bath at 100° C. to the water in the calorimeter need not be considered at present. It is the result of the arrangement adopted for heating the copper, and is not necessarily incidental to the use of the calorimeter in the method of mixtures.

There are, however, two important sources of error inseparable from the method. The vessel containing the water is protected as far as possible by the construction of the calorimeter from loss or gain of heat by conduction or radiation during the process of mixing. There must, however, always be some loss or gain of heat in this way during an experiment, and if the experiment happens to be a lengthy one the loss or gain may be appreciable. This source of error can be practically eliminated by arranging that, in any experiment, the final temperature of the water in the calorimeter shall be as much below, or above, the temperature of the surroundings as the initial temperature of the water is above, or below, it. The mean temperature of the water during the experiment is thus the same as the temperature of the surroundings, and the loss or gain of heat by the calorimeter during the first half of the experiment is practi-

cally compensated for by the corresponding gain or loss during the second half.

When this method of elimination cannot be adopted, the error can be corrected for by determining the mean rate of "cooling" or "heating" during the experiment, and applying the necessary correction to the final temperature. Thus, if the water in the calorimeter cools at the rate of r degrees per second just before the experiment begins, and at the rate of r' degrees per second just after it ends, then the mean rate of cooling during the experiment is $\dfrac{r + r'}{2}$ degrees per second, and if the experiment lasts for n seconds, then the final temperature should obviously be taken $\dfrac{n(r + r')}{2}$ degrees higher than the value observed.

In general, however, r, r', and n are so small that the correction may, in most cases, be neglected. The method of eliminating the error referred to above evidently makes r and r' equal, but of opposite sign, so that $(r + r')$ is zero, and the error vanishes.

Numerical Example. — In an experiment similar to Exp. 31 above, the temperature of the water in the calorimeter is found to rise ·3° in five minutes just before the experiment begins and to fall 1·5° in five minutes immediately after the experiment is over; the experiment lasts 40 seconds, and the final temperature is observed to be 26·4° C., find the corrected value of this temperature.

The rate of *rise* of temperature at the beginning of the experiment is ·001° per second, and the rate of *fall* of temperature at the end of the experiment is ·005° per second. The mean rate of change of temperature during the experiment is, therefore, a fall of ·002° per second, and the total "cooling" effect during the experiment is sufficient to cause a fall of 40 × ·002°, or, ·08°. The corrected value of the final temperature is, therefore, 26·48° C., for if there had been no cooling during the experiment the temperature would evidently have risen ·08° higher than it did.

A more serious source of error arises out of the fact that the quantity of heat lost or gained by the *water* in the calorimeter

is not the full measure of the heat lost or gained by the calorimeter. The vessel containing the water, and the thermometer and stirrer in it change temperature with the water, and gain and lose heat as the water gains and loses heat. This error is minimised by making the calorimeter vessel of very thin material, so that its mass is small, and by selecting a thermomometer and stirrer of small mass. The heat gained or lost by the vessel and its accessories can thus be made a small proportion of the quantity gained or lost by the water, particularly if the mass of the water is considerable. The heat gained or lost by the calorimetric apparatus cannot, however, be neglected, and it is necessary, even in comparatively rough experiments, to apply a correction for it.

This correction may, evidently, be made by taking the mass of the water to be greater than its actual value by a small amount, such that the heat gained or lost by this additional mass is the exact equivalent of the heat gained or lost by the calorimeter vessel and its accessories.

The heat gained or lost by the increased mass of water will thus be exactly equal to the heat gained or lost by the actual mass of water and the calorimetric apparatus combined, and the additional mass of water may, therefore, be considered as the **water equivalent** of the calorimetric apparatus.

Thus, let the mass of water in the calorimeter be m grammes, and let the *change* of temperature observed in an experiment be $t°$, then the heat gained or lost by the calorimeter is not mt units, but $(mt + x)$ units, where x denotes the number of units gained or lost by the vessel and its accessories. Now, if m be supposed to be increased by a small additional mass w, such that

$$(m + w)\, t = mt + x,$$

then wt is the exact equivalent of x, and w is the **water equivalent** of the calorimeter.

In order to make correction for this error it is, therefore, necessary to determine the water equivalent of the calorimeter. This determination is usually made experimentally by the following method.

Experiment 32. —Set up the calorimeter ready for use, fill it about one-third full of water at a temperature about 10° higher than the temperature of the room, and find the weight of the water in the usual way. Let the weight of the water be 112·4 grammes.

Take about an equal quantity of water in a beaker at a temperature about 10° below the temperature of the room. Then after taking the temperatures of the water in the calorimeter and the water in the beaker, very carefully mix the two quantities of water by pouring the quantity in the beaker quickly into the calorimeter. Stir the water during the mixture and note the final temperature. Then weigh the calorimeter again to determine the mass of water added from the beaker. Let the temperature of the water in the calorimeter be recorded as 23·4° C., and that of the water in the beaker as 8·1° C. Also, let 16·4° C. be the final temperature observed, and let the mass of water poured from the beaker into the calorimeter, be found to be 101·2 grammes.

Then, if w grammes of water be the water equivalent of the calorimeter, the heat lost by the calorimeter is

$$(112\cdot4 + w)\,(23\cdot4 - 16\cdot4) \text{ units, or}$$
$$(112\cdot4 + w)\,(7) \text{ units.}$$

Also, the heat gained by the water added from the beaker is

$$101\cdot2\,(16\cdot4 - 8\cdot1) \text{ units, or}$$
$$101\cdot2 \times 8\cdot3 \text{ units.}$$

Now, these two quantities of heat are equal, so that

$$(112\cdot4 + w)\,7 = 101\cdot2 \times 8\cdot3, \text{ or}$$
$$w = 7\cdot6 \text{ nearly.}$$

That is, the water equivalent of the calorimeter is 7·6 grammes.

It should be noted that it requires very great care to get a reliable result in this experiment.

When the water equivalent of a calorimeter is known, it can obviously be used in working out the results of any experiment with the calorimeter. It must be remembered, however, that the water equivalent of a calorimeter is not a constant. Its

value depends to some extent upon the nature of the experi-
ment; thus, the water equivalent for an experiment in which a
small quantity of water is used, must be somewhat less than the
water equivalent for an experiment in which the vessel is nearly
filled with water. The vessel and its accessories are obviously
more fully involved in the mixing in the second experiment.

The method of working out the result of a calorimetric
experiment, in which the water equivalent of the calorimeter is
known, is illustrated by the following example.

Numerical Example.—Let the water equivalent of the calorimeter
used in Exp. 31 be taken as 10 grammes.

Then, from the data of the experiment, the heat gained by the
calorimeter is (150 + 10) (21·1 − 14·6) units, or 160 × 6·5 units, and
the average quantity of heat lost by 1 gramme of copper in cooling
through 1° is, therefore, given by

$$\frac{160 \times 6\cdot5}{124\cdot3 \times 78\cdot9} \text{ unit, or } \cdot106 \text{ unit.}$$

It will be found that most of the calorimetric measurements
dealt with later are made by the method of mixtures.

CHAPTER VII.

SPECIFIC HEAT.

38. Thermal Capacity.—The quantity of heat given out by unit mass of copper in cooling through 1° was found by the method described in Exp. 31 to be about a tenth of a unit of heat. If the experiment is repeated under reversed conditions so that a piece of cold copper wire is mixed with hot water, it will be found that the quantity of heat required to raise 1 gramme of copper has, as we should expect, exactly the same value. If, further, the experiment be repeated a number of times with different pieces of copper, it will be found that the result obtained is practically the same in all cases.

The quantity of heat which 1 gramme of copper gains or loses for one degree change of temperature is thus a constant characteristic of the substance. This constant is called the **thermal capacity**, or the heat capacity of copper.

If the experiment is carried still further and repeated for a number of *different* substances, it will be found that while the thermal capacity of any given substance has a definite constant value, the values obtained for different substances are different.

The **thermal capacity** of a substance is, therefore, a characteristic constant of the substance, and may be defined as the quantity of heat which unit mass of the substance gains or loses for one degree change of temperature.

The mean thermal capacity of a substance for any given change of temperature is the mean or average quantity of heat which unit mass of the substance gains or loses *per degree* for that change of temperature.

The thermal capacity of water is, by definition, one unit of heat, for the unit of heat is defined as the quantity of heat required to raise 1 gramme of water through one degree.

The thermal capacity of a substance is usually determined experimentally by determining its specific heat (Art. 39) by the method indicated in Exp. 31, and described in fuller detail below in Art. 40. The thermal capacities of different substances may, however, be compared and determined roughly by the method indicated in the following experiments. The experiments cannot give accurate results, but they serve to illustrate in a roughly quantitative manner that different substances may have very different thermal capacities.
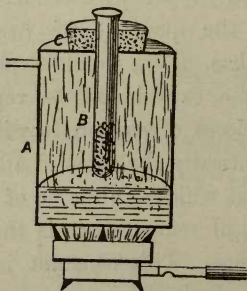
Fig. 43.

Experiment 33.—Take 100 grammes of iron (small nails or wire) at 100° C., and mix it with 100 grammes of water at the ordinary temperature in a beaker arranged as described in Exp. 31. The iron may be conveniently heated in a *heater* of the form shown in Fig. 43. It consists of a copper can, A, which serves as a small boiler, and a large test-tube, or boiling-tube, B, in which the substance to be heated is placed. The top of the can is flat, and has a central hole about an inch in diameter in it. The tube is fitted through a wide flat cork about one and a half inches in diameter so that when it is passed through the hole in the top of the can, the cork rests on the top and supports the tube in the manner shown in the figure. When water is boiled in the can the upper part of it is filled with steam, which thus surrounds the tube, and heats any substance which may be placed in it for that purpose.

When it is desired to remove the substance the tube can be lifted by the cork, and the substance in it can be transferred quickly and easily into any other vessel.

When the iron and water are mixed note the final temperature.

Let the temperature of the water before mixing be recorded as 10° C., and the final temperature as 19° C.

Here it will be seen that 100 grammes of iron in cooling through 81° give out a quantity of heat sufficient to raise *the same mass* (100 grammes) of water through 9°.

The thermal capacity of iron is, therefore, $\frac{9}{81}$, or $\frac{1}{9}$, the thermal capacity of water. That is, the thermal capacity of iron is about $\frac{1}{9}$ calorie, or ·11 calorie.

It will be evident from this example that when *equal masses* of any two substances at different temperatures are "mixed," the changes of temperature of the substances are inversely proportional to their thermal capacities. Thus, in the case of iron and water above, the ratio of the thermal capacity of iron to the thermal capacity of water is the ratio of 9 to 81, or 1 to 9.

Experiment 34.—Mix 100 grammes of lead shot at 100° C. with 100 grammes of water at 10° C., and note the final temperature. It will be found to be about 12·5°.

The thermal capacity of lead is, therefore, about $\frac{5}{175}$, or $\frac{1}{35}$ of the thermal capacity of water. That is, the thermal capacity of lead is about $\frac{1}{35}$ calorie, or ·03 calorie.

Experiment 35.—Mix 100 grammes of aluminium at 100° C. with 100 grammes of water at 10° C., and note the final temperature. It will be found to be about 25° C.

The thermal capacity of aluminium is, therefore, about $\frac{15}{75}$, or $\frac{1}{5}$ that of water, or about ·2 calorie.

Experiment 36.—Mix 100 grammes of mercury at 100° C. with 100 grammes of water at 10° C., and note the final temperature. It will be found to be about 13° C.

The thermal capacity of mercury is thus about $\frac{3}{87}$, or $\frac{1}{29}$ that of water, or about ·034 calorie.

Experiment 37.—Mix 100 grammes of water at 40° C. with 100 grammes of glycerine at 10° C. (pour the water into the glycerine), and note the final temperature. It will be found to be about 20° C.

The thermal capacity of glycerine is thus about $\frac{10}{20}$, or one-half that of water, or about ·5 calorie.

It is sometimes convenient to speak of the thermal capacity of a body, or the thermal capacity of a piece of apparatus as a whole, when the quantity of heat required to raise the body or the apparatus through one degree is meant.

39. **Specific Heat.**—The **specific heat** of a substance is the ratio of its thermal capacity to the thermal capacity of water. The thermal capacity of water is, however, the unit of heat, and if this be understood, the specific heat of a substance may be defined as the number of units of heat required to raise unit mass of the substance through one degree.

Thus, if the thermal capacity of the substance is s units, and the thermal capacity of water is 1 unit, the specific heat of the substance is the ratio $\dfrac{s \text{ units}}{1 \text{ unit}}$, and its value is, therefore, given by s, the number which measures the thermal capacity of the substance.

It must be remembered, however, that the specific heat of a substance is the *ratio* of two fixed quantities of heat. It is, therefore, a number involving no unit, and its value is constant and quite independent of the unit in which the quantities of heat are measured.

The **mean specific heat** of a substance for a given range of temperature is the mean or average number of units of heat required to raise 1 gramme of the substance through one degree over the given range. Thus, if Q units of heat are required to raise m grammes of a substance from t'° C. to t° C., then $\dfrac{Q}{m\,(t - t')}$ is the mean specific heat of the substance between t'° C. and t° C. Similarly, if s denote the mean specific heat of a substance between t'° C. and t° C., the number of units of heat required to raise m grammes of the substance from t'° C. to t° C., or given out by m grammes of the substance in cooling from t° C. to t'° C., is given by $m\,s\,(t - t')$.

Numerical Example.—If a mass of copper weighing 20 grammes

requires 180 units of heat to raise it from 10° C. to 100° C., the mean specific heat of copper between 10° C. and 100° C. is $\frac{180}{20 \times 90}$ or ·1.

Also, assuming this value of the mean specific heat, the number of units of heat required to raise 50 grammes of copper from 10° C. to 100° C. is 50 × 90 × ·1, or 450.

40. Experimental Determination of the Specific Heat of a Substance.

—The most important method of determining the specific heat of a substance is the method of mixtures. A weighed mass of the substance whose specific heat is to be determined, is heated to a known temperature and mixed with the water in a water calorimeter. The final temperature of the mixture is then noted, and the specific heat is calculated from the data of the experiment.

Fig. 44.

The essential apparatus for the determination of specific heat by this method is, therefore, a calorimeter, with the necessary accessories, and a heater for heating the weighed mass of the substance to the required temperature. A simple form of heater, shown in Fig. 43, is described in Exp. 33, but the form most generally used for specific heat work is that shown in Fig. 44. It is made of copper, and consists as shown in the section given in the figure, of two coaxial cylinders with the space between closed in at each end to form a hollow cylindrical vessel about 20 cms. long, and about 10 cms. external and 5 cms. internal diameter.

The vessel is fitted with inlet and exit tubes so that a current of steam can be passed through the space between the cylinders, and the outer surface is covered with a coating of felt to prevent undue condensation of the steam by the cooling effect of the
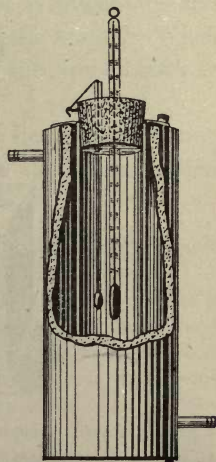
outer air. The central space enclosed by the inner cylinder can thus be surrounded by steam, and serves as an oven or heating space in which any small object can be heated practically to 100° C. This space is closed at the top by a cork, and at the bottom by a sliding shutter of wood or felt, and a thermometer is fitted through the cork so that the bulb and a good part of the stem are within the space. The weighed mass of the substance whose specific heat is to be determined, is suspended in this space by a silk fibre or thread, so that it hangs near the
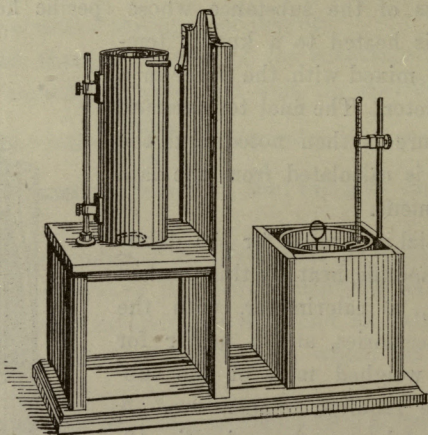
Fig. 45.

bulb of the thermometer. The fibre or thread used for this purpose passes through a short length of fine bore tubing fitted through the cork, and is attached to a small hook fixed to the edge of the cork. When the substance is heated to the temperature of the heating space it can evidently be lowered by means of the suspension thread into a calorimeter placed immediately below it, without undergoing any appreciable loss of heat in transit.

In the general arrangement of the apparatus, it is important to provide for the speedy transfer of the heated substance

from the heater to the calorimeter, and at the same time to protect the calorimeter from any heating effect due to the heater. The form of apparatus designed by Regnault for this purpose is shown in Fig. 45. It consists of a calorimeter and a heater of the type just described, mounted on a solid base board. The calorimeter is not, however, stationed immediately below the heater. It is set up on a slide at the other end of the base board, and is separated from the heater by a wooden screen arranged as a sliding shutter between them. When it is required to transfer the heated substance from the heater to the calorimeter, the sliding shutter is drawn up, and the calorimeter is run in on its slide under the heater. When the transfer is effected, the calorimeter is at once drawn back to its place, and the shutter is lowered.

The general method of making a specific heat determination is indicated by the following experiment for the determination of the specific heat of brass.

Experiment 38.—Set up the heater and calorimeter ready for use. Take about 100 grammes of brass in any convenient form.

It is preferable to take brass wire or thin sheet brass, but brass is a good conductor, and readily gains and loses heat (while heating and mixing) even in a solid piece. When, however, the substance is a bad conductor of heat, it must be taken in small pieces, or in some form offering a large surface in proportion to its mass.

Weigh the brass and suspend it in the heater. Let the weight taken be 102·2 grammes (it is evidently unnecessary in this case to weigh beyond the first, or at most the second, place of decimals).

Find the weight of the water in the calorimeter, and, if necessary, determine the water equivalent. Let the weight of water be 150·2 grammes, and let the water equivalent be 4·8 grammes.

When the temperature indicated by the thermometer in the heater is quite steady, stir the water in the calorimeter, and record its temperature. Then place the calorimeter below the heater, drop the hot brass into it, and remove it at once. Stir the water in the calorimeter during the mixture, and record the final temperature.

Let the temperature in the heater be recorded as 97·6° C., the initial temperature of the water in the calorimeter as 13·2° C., and the final temperature after mixing as 17·7° C.

From these data the specific heat of brass can now be calculated.

For if s denote the specific heat of brass, then the heat lost by the brass

$$= 92 \cdot 2 \ (97 \cdot 6 - 17 \cdot 7) \ s \ \text{calories.}$$
$$= 92 \cdot 2 \times 79 \cdot 9 \times s \ \text{calories.}$$

The heat gained by the water and the calorimetric apparatus

$$= (150 \cdot 2 + 4 \cdot 8) \ (17 \cdot 7 - 13 \cdot 2) \ \text{calories.}$$
$$= (155 \times 4 \cdot 5) \ \text{calories.}$$

The temperature of the room during the experiment was found to be $15 \cdot 5°$ C., so that no correction for cooling during the experiment is necessary.

We therefore have

$$92 \cdot 2 \times 79 \cdot 9 \times s = 155 \times 4 \cdot 5,$$

or
$$s = \frac{155 \times 4 \cdot 5}{92 \cdot 2 \times 79 \cdot 9} = \cdot 095.$$

The specific heat of brass is, therefore, given by this experiment to be $\cdot 095$.

It is important to notice that in this experiment, and in all calorimetric experiments of the same type, the accuracy of the result obtained depends almost entirely on the accuracy with which the change of temperature of the water in the calorimeter is obtained. The change here is only $4 \cdot 5°$, and it is obtained by *two* readings, so that an error of only a tenth of a degree in each reading *may* introduce an error of over 4 per cent. If a thermometer with a fairly open scale reading to tenths of a degree is used, it is possible to estimate hundredths of a degree, and the error in reading need not exceed one-hundredth of a degree. Even this error, however, may introduce an error of $\cdot 02°$ in the *change* of temperature observed, and if this change is small the *percentage* error may be great.

It is evident, therefore, that very great care must be taken in reading the temperatures to be observed in an experiment of this kind, and that the experiment should be so arranged that the changes of temperature to be found are not too small in proportion to the possible error in determining them.

It will now be understood that although it is quite easy to determine the weights involved in the experiment to 1 in 100,000, it is waste of time to weigh with greater accuracy than 1 in 1,000 at most.

The method detailed in the foregoing experiment applies only to the case of a solid which can be immersed in water without effect of any kind.

If the substance is soluble in water, or is affected in any way by immersion in water, the simplest method to adopt for the determination of its specific heat is to use in place of water in the calorimeter some other liquid of *known* specific heat, in which the solid can be immersed without injury. The determination can then be made exactly in the manner described above.

The determination can also be made by enclosing the solid in a glass bulb or in a thin metal flask, and adopting the usual method for a solid which can be immersed in water. The thermal capacity of the glass or metal envelope can easily be allowed for in reducing the results.

A third method which can be adopted with solids which cannot be directly immersed in water, is to use a water calorimeter in which the vessel containing the water is fitted with a small inner vessel, into which the substance can be dropped when heated. This inner vessel is surrounded by the water in the calorimeter, so that the exchange of heat during the process of mixing readily takes place through its walls, and its presence is allowed for in calculation by making the necessary addition to the water equivalent of the calorimeter.

The **specific heat of a liquid** may also be determined by the method of mixtures in the same general way as a solid. It is necessary, however, to adapt the details of the method to the liquid form of the substance.

The method described in Exp. 38 may be adopted for the determination of the specific heat of a liquid by placing the liquid in the calorimeter and using a solid of *known* specific heat as the substance to be heated and mixed with the liquid.

Numerical Example.—In an experiment for the determination of the specific heat of aniline 45·2 grammes of glass (specific heat ·192) at 100° C. were mixed with 150·1 grammes of aniline at 12° C., and the final temperature after mixing was found to be 20·7° C. The water equivalent of the calorimeter was known to be 4 grammes.

The specific heat of aniline can at once be calculated from these data.

The heat lost by the glass in cooling from 100° C. to 20·8° C. is

$$(45\cdot2 \times \cdot192 \times 79\cdot2) \text{ calories},$$

or,   687·3 calories.

The heat gained by the aniline and the calorimeter is

$$\{ (150\cdot1 \times 8\cdot7 \times s) + (4 \times 8\cdot7) \} \text{ calories},$$

or, $(1305\cdot87\,s + 34\cdot8)$ calories ;

where s denotes the specific heat of aniline, we therefore have :

$$1305\cdot87\,s + 34\cdot8 = 687\cdot3,$$

or, $1305\cdot87\,s = 652\cdot5.$

Therefore, $s = \dfrac{652\cdot5}{1305\cdot87} = \cdot5.$

That is, the specific heat of aniline given by the experiment is ·5.

When this method cannot be adopted, one of the methods suggested above for a solid which cannot be immersed in water may be employed. The liquid may be sealed into a glass bulb or a thin metal envelope, and its specific heat determined as in the case of a solid. Or, the liquid may be heated in a special chamber in the heater, and then run out, through a tube specially provided for the purpose, into an inner vessel in the calorimeter. This method was used by Regnault in his researches on the specific heat of liquids.

The specific heat of gases is a subject which presents difficulties in theory and in experimental detail which cannot here be considered.

It may be noticed, however, that a gas has two specific heats according as it undergoes change of temperature at constant pressure or at constant volume. The *specific heat at constant pressure* is greater than *the specific heat at constant volume*, because the heat supplied to the gas is required, at constant pressure, not only to produce rise of temperature, but also to supply the energy required by the gas to do work in expanding against external pressure. When a gas is heated at constant volume there is no expansion, and consequently no energy is expended in doing work against external pressure.

Regnault determined the specific heats of a number of gases at constant pressure by an adaptation of the method of mixtures. The gas was passed from a reservoir, where it was stored at high pressure, through a spiral coil immersed in an oil bath, where it was heated to a high known temperature, and then through a special vessel immersed in the water of the calorimeter. From this vessel it escaped into the open air, but the vessel was so constructed that the gas passed through so slowly that it was cooled to the temperature of the water in the calorimeter before escaping. In this way a known mass of the gas was heated to a known temperature, and then made to give up in the calorimeter, under constant atmospheric pressure, the heat it lost in cooling through a known range of temperature. The mass of the gas was determined by noting the change of pressure in the reservoir, the temperature to which it was heated was given by the thermometer in the oil-bath, and the heat given up in cooling to the *mean* temperature of the water in the calorimeter, was measured by the calorimeter in the usual way.

Regnault found that the specific heat of a gas at constant pressure was practically the same at all pressures.

41. Table of Specific Heats.—The table gives the mean specific heats of a number of common substances for the range of temperature specified in the third column for each substance.

SOLIDS.

Substance.	Mean Specific Heat.	Range of Temperature.
Aluminium, . . .	·2122 . . .	15° C. – 100° C.
Copper, ...	·0933 . . .	15° C. – 100° C.
Gold, ...	·0316 . . .	0° C. – 100° C.
Iron, ...	·1124 . . .	0° C. – 100° C.
Lead, ...	·0315 . . .	20° C. – 50° C.
Nickel, ...	·1092 . . .	15° C. – 100° C.
Platinum, ...	·0323 . . .	0° C. – 100° C.
Silver, ...	·0559 . . .	0° C. – 100° C.
Tin, ...	·0559 . . .	0° C. – 100° C.
Zinc, ...	·0935 . . .	0° C. – 100° C.

SOLIDS.—*Continued.*

Substance.	Mean Specific Heat.	Range of Temperature.
Brass, ...	·086	15° C. – 100° C.
Glass, ...	·196	0° C. – 100° C.
Ice, ...	·504	– 20° C. – 0° C.
Quartz, ...	·191	0° C. – 100° C.

LIQUIDS.

Mercury, ...	·0336	15° C. – 100° C.
Alcohol, ...	·61	0° C. – 50° C.
Oil of turpentine, . .	·45	0° C. – 100° C.
Ether, ...	·54	0° C. – 30° C.
Aniline, ...	·49	0° C. – 50° C.
Glycerine, ...	·56	15° C. – 20° C.
Benzine, ...	·38	0° C. – 50° C.

GASES.

Mean Specific Heat at Constant Pressure.

Air, ...	0·237
Oxygen, ...	0·217
Nitrogen, ...	0·244
Hydrogen, ...	3·409
Carbon monoxide, ...	0·245
Carbon dioxide, ...	0·216
Steam, ...	0·481

CHAPTER VIII.

LIQUEFACTION AND SOLIDIFICATION.

42. Liquefaction and Solidification.—The process by which a solid changes, when heated, from the solid state to the liquid state, is called **liquefaction** or **fusion**, and the reverse process by which a liquid changes when cooled from the liquid state to the solid state is called **solidification** or **freezing**.

The experimental study of this change of state in any substance involves the determination of the temperature changes, the volume changes, and the heat changes which accompany the change.

It is now known that, in the case of all elementary substances, and many compound substances, a given substance may, under suitable temperature conditions, exist as a solid, a liquid, or a gas. It is also known that the change from one state to another is effected by heating or cooling the substance. The changes from the solid state to the liquid state, and from the liquid state to the gaseous or vapour state, are produced by heating, and the reverse changes from the vapour state to the liquid state, and from the liquid state to the solid state by cooling.

Thus, water exists as a definite chemical substance in the solid state as ice, in the liquid state as water, and the vapour state as water vapour or steam, and it is a matter of common knowledge that the changes from ice to water, and from water to steam, are effected by heating the substance, while the reverse changes from steam to water, and from water to ice, are effected by cooling the substance.

43. The Melting Point.

—The temperature effects which accompany liquefaction and solidification are conveniently studied by the method of the following experiment.

> **Experiment 39.**—Fill a small beaker or flask about half full of naphthalene, and heat it on a water bath until the substance is completely liquefied. Turn off the burner used for heating the bath. Then place a thermometer reading from 0° C. to 100° C. with its bulb in the liquefied substance in the beaker, and allow the substance to cool slowly on the bath. Note the temperature at intervals of a minute or so as the cooling proceeds, until some time after solidification is observed to be complete.
>
> Then relight the burner, and adjust it so as to raise the temperature of the bath very slowly, and note the temperature as before, at intervals of a minute or so, as the temperature rises, until the substance is again completely liquefied.
>
> It will be found on examining the data that during the first part of the experiment the temperature of the substance as a liquid falls steadily until *solidification begins ; it then remains constant throughout the process of solidification at* 79° C., and when the process is complete the temperature of the substance now in the solid state again falls. Also, in the second part of the experiment the temperature of the substance rises until *liquefaction begins ; it then remains constant throughout the process of liquefaction at* 79° C., and when the process is complete the temperature of the substance now in a liquid state again rises.
>
> It should be noted that in an experiment of this kind the substance must be heated and cooled very slowly in order that the temperature at any instant may be uniform throughout the mass of the substance.

This experiment shows that in the case of the change of state from liquid to solid, and the change from solid to liquid, both take place at the same temperature, and that this temperature is constant throughout the process in each case.

Experimental research shows that the result here obtained for a particular substance is true generally for all substances which crystallise in solidifying. That is, when a substance changes state from solid to liquid, or from liquid to solid, the change takes place at a definite fixed temperature, which remains constant throughout the process. This temperature is called **the**

melting point of the substance.   The fact that the temperature of the substance remains constant throughout the process of solidification or liquefaction, evidently implies that the liquid and solid are throughout the change *at the same temperature*.   This fact is well illustrated by the following experiment with ice and water.

> **Experiment 40.** — Partly fill a beaker with small pieces of ice and water.   Place a stirrer and a thermometer in the beaker, and heat the mixture of ice and water gently.   Stir the mixture carefully, and note the temperature indicated by the thermometer as the heating proceeds.
>
> It will be found that the temperature remains quite constant at 0° C. until the *whole* of the ice is melted ; it then begins to rise.
>
> It will be found an advantage in carrying out this experiment to sink a number of pieces of ice to the bottom of the beaker by weighting them with lead wire, or by placing them under a flat ring or disc of thin sheet lead.

In the case of substances such as iron, glass, wax, fats, and other substances which are non-crystalline or amorphous in the solid state, experiment shows that the change from the solid to the liquid, or from the liquid to the solid, is not so well defined as in a crystalline substance.   In changing state the substance generally passes through a *plastic state*, which may extend over a considerable range of temperature.   The process of fusion or solidification thus becomes a gradual process, taking place within certain limits of temperature, instead of a sharply-defined change taking place at a definite fixed temperature.   An amorphous solid cannot, therefore, be said to have a definite melting point.   In some substances, however, the limits of temperature within which change of state takes place are very narrow, so that the mean temperature at which the change takes place may be taken as the melting point.   In other substances the limits are so widely separated that no definite melting point can be given.

Experiment 41.—Repeat Exp. 40 with sealing wax or pitch instead of naphthalene.

It will be found that both during solidification and fusion the temperature is not constant, but changes slowly as the process proceeds.

If the experiment is tried with paraffin wax it will be found that the temperature limits of the plastic state are so narrow that the mean of the limits may be taken as the melting point of the substance.

Thus, in an actual experiment the change of state was found to take place between 52·3° C. and 52·8° C., so that 52·5° C. may be assigned as the melting point of the wax.
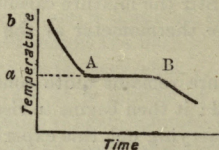
Fig. 46.
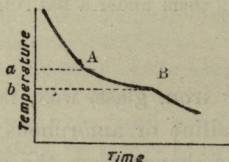
Fig. 47.
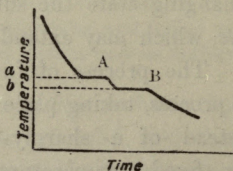
Fig. 48.

Fig 49.

In the case of a substance such as an alloy, which is a mixture of several different substances, the process of fusion or solidification may extend over a considerable range of temperature, and the temperature may be constant for some time at more than one point during the process.

The difference in the behaviour of different substances during fusion or solidification is very clearly brought out by plotting

curves for typical substances, showing in each case the change of temperature with time as the substance is heated or cooled through a range of temperature, including the melting point of the substance.   The data for plotting a curve of this kind are obtained in the manner described in Exp. 40.   Thus, Figs. 46-48 show for a crystalline substance, an amorphous substance, and an alloy, respectively, the fall of temperature with time as the substance changes state from liquid to solid in cooling.   In each figure the points A and B indicate, respectively, the beginning and end of the change of state.   Also, in Fig. 46 the temperature indicated at *a* is the melting point, and in Figs. 47 and 48 the range of temperature indicated by *a b* is evidently the range within which the change of state takes place.

The melting point of a substance may be determined by the method of Exp. 40.   An oil bath or sand bath may be used for substances melting at temperatures above 100° C.

If the substance has a definite melting point the determination is made by noting the temperature at which the substance remains *constant* during change of state.

If the substance has no well-defined melting point, it is best to plot a curve, as explained above, showing the range of temperature within which the change takes place, and indicating the progress of the change.

When only a small quantity of the substance is available, the melting point is most conveniently determined by the method of the following experiment.

Experiment 42.—Determine the melting point of the given substance by the method described below.   Draw out a piece of glass tubing so as to obtain a very thin-walled tube about a millimetre in diameter.   Cut off a piece of this tube about 5 cms. long, and close it at one end.

Then fill the bottom third of this tube with the given substance, and attach the tube to the bulb of a thermometer by small rubber rings (snipped off a piece of small bore rubber tubing) as shown in Fig. 49.

9

Now immerse the bulb of the thermometer and the greater part of the attached tube in water, melted paraffin wax, or oil (according to the temperature required), in a glass beaker, and heat the liquid slowly.

Watch the substance in the tube as the temperature rises, and when liquefaction begins stop heating, and note the temperature indicated by the thermometer. This temperature is probably higher than the melting point, for it will generally be found that although the heating is stopped, the substance will liquefy completely, and may remain liquid for some degrees fall of temperature.

As the temperature falls stir the bath carefully, and note the temperature at which the substance begins to solidify.

Allow the substance to solidify, then heat the bath gently so as to raise the temperature *very slowly*, and note the temperature at which the substance begins to liquefy. These two temperatures should not differ by more than half a degree. If they do, repeat the two observations until the temperatures obtained show a very small difference.

The mean of these two temperatures may be taken as the melting point of the substance.

The determination of very high and very low melting points requires special apparatus and special methods which cannot here be considered.

Table of Melting Points.

Platinum,	1,710° C.	Glass,	1,100° C.
Iron,	1,503	Potassium sulphate,	1,070
Copper,	1,062	Borax,	1,000
Gold,	1,064	Common salt,	800
Silver,	955	Sulphur,	115
Aluminium,	657	Naphthalene,	79
Zinc,	419	Phosphorus,	44
Lead,	327	Paraffin wax,	54
Tin,	232		
Mercury,	− 39		
Hydrogen,	− 260	Ice,	0

44. Change in Volume at Change of State.—It is to be expected that the density of a given substance in the solid state will differ from its density in the liquid state. It is, therefore,

probable that a given mass of any substance will undergo change of volume in changing from solid to liquid, or from liquid to solid.

> **Experiment 43.**—Melt a quantity of paraffin wax in a large evaporating basin, and then allow it to solidify. It will be found that the surface of the mass of solid wax is not flat, but shows a considerable concavity caused by the contraction of the substance in changing from the liquid to the solid state.
>
> Paraffin wax, therefore, expands on melting, and contracts in solidifying.

> **Experiment 44.**—Melt some lead in an iron ladle or small melting pot and allow it to solidify.
>
> The surface of the solid lead will be found to be concave, as in the case of the wax. That is, lead also expands on melting and contracts on solidifying.

> **Experiment 45.**—Fill an expansion flask (Fig. 2) with small pieces of ice and water, so that the water column in the tube stands at rather a high level.
>
> Place the flask in a bath of warm water, and notice how the volume of the ice and water in the flask changes as the ice melts.
>
> It will be found that as the ice in the flask melts the level of the water in the tube falls rapidly, thus showing that the volume of the water produced by the melting of the ice is *less* than the volume of the ice melted.
>
> That is, ice contracts on melting, or water expands in freezing.

These experiments suggest that certain substances, such as wax and lead, expand in melting, and that others, like ice, contract in melting. A general experimental study of the subject shows that, as a general rule, a substance expands in melting and contracts in solidifying. Water is, however, a notable exception to this rule, for water expands in freezing and contracts in melting. Iron, bismuth, and few other substances, are also exceptions to the general rule, and behave in the same way as water.

It has been shown that if water is sufficiently cooled in a closed vessel the force exerted by it in expanding as it freezes

may be great enough to burst the vessel. Major Williams, experimenting in 1784, showed that strong steel shells could be burst in this way. This explains how water pipes may be burst during a frost. The water in a section of the pipe freezes, and the expansion thus produced may be sufficient to burst the pipe at some point in the section; then when a thaw sets in, and the ice in the pipe melts, a serious leak takes place at the point of bursting.

In the same way tree trunks and plant cells containing moisture may be burst and destroyed during frosty weather.

The weathering action of frost on rocks and soils is also due to this same cause. Water finds its way into the cracks and crannies of rocks, and fills up the interstices of the soil. When this water freezes the expansion breaks down the rock and disintegrates the soil, which is thus made more workable and more fertile.

The metals and alloys which expand in solidifying are specially suitable for casting. The expansion of the metal at solidification forces it to take a sharp and clear impression of the inner surface of the mould, and so produces a sharp, well-defined casting.

The quantitative determination of the change of volume which accompanies the fusion or solidification of any given substance presents great difficulties. Determinations have been made for a number of substances by an adaptation of the dilatometer and weight-thermometer methods, and also by determining the density of the substance in the solid and liquid states.

In the case of water, it is found that the volume of a gramme of water at 0° C. is about 1·0001 c.c., while the volume of a gramme of ice at the same temperature is 1·0908 c.c. The expansion which takes place when one gramme of water freezes is thus about ·0907 c.c. That is, the expansion is almost exactly one-eleventh of the volume occupied by the water.

The change in volume which takes place in one gramme of

water substance between — 8° C. and 10° C. is shown by the curve ABCD in Fig. 50. The portion AB shows the expansion of the substance as ice between − 8° C. and 0° C., and the portion CD shows its change of volume as water between 0° C. and 10° C. The comparatively large decrease in volume indicated by the portion BC at 0° C. is the change in volume which takes place in changing from ice at 0° C. to water at 0° C. There is some experimental evidence that the changes in volume at B and C
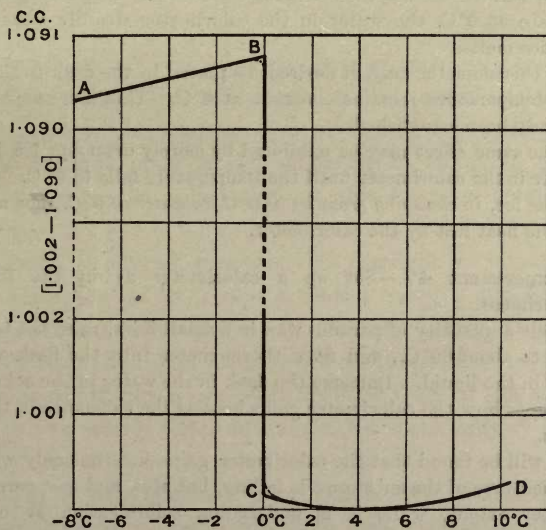
Fig. 50.

do not take place abruptly at 0° C. but gradually, as indicated by the dotted curves at these points, within a small range of temperature below 0° C. for the changes at B and above 0° C. for the change at C. That is, the portions AB, BC, and CD of the curve ABCD are probably continuous and not discontinuous at the points B and C.

45. **Latent Heat of Fusion.**—It has already been noticed that when a substance fuses or liquefies it absorbs heat during

the process without showing any change of temperature. Also when a substance solidifies it gives out heat during the process without showing any fall of temperature. These facts are further illustrated by the following experiments :—

Experiment 46.—Set up a water calorimeter ready for the measurement of heat. Let the temperature of the water in the calorimeter be about 20° C. Half fill a small flask with small pieces of ice and water and place the flask in the water in the calorimeter.

It will be found that although the water and ice in the flask remain at 0° C. the water in the calorimeter steadily loses heat as the ice melts.

A thermometer may, if desired, be placed in the flask to show that the temperature remains constant at 0° C. This fact has, however, already been established.

The same effect may be exhibited by merely dropping ice into the water in the calorimeter until the temperature falls to 0° C.

The ice, *in changing from ice at 0° C. to water at 0° C.*, has absorbed all the heat lost by the calorimeter.

Experiment 47.—Set up a calorimeter as in the foregoing experiment.

Melt a quantity of paraffin wax in a small flask, raise the temperature to about 60° C., and fit a thermometer into the flask with its bulb in the liquid. Immerse the flask in the water in the calorimeter and note how the calorimeter gains heat as the substance in the flask cools.

It will be found that the calorimeter gains heat not only while the temperature of the substance is falling, but also, and to a perceptibly greater extent, while it is undergoing solidification at constant temperature.

The heat thus absorbed at constant temperature during fusion, and evolved at constant temperature during solidification, is known as the *latent heat of fusion.* The term *latent* is due to the early philosophers who thought that the heat absorbed without rise of temperature during fusion became latent or hidden in the liquid, and reappeared again when the liquid solidified. It is now known that heat is a form of energy, and that the latent heat absorbed by any substance during fusion is converted into

molecular potential energy and supplies the increase of molecular potential energy which accompanies the change from the solid to the liquid state.

The quantity of heat absorbed by unit mass of a given substance, in changing from the solid to the liquid state at the melting point of the substance, is found to be constant and exactly the same as the quantity evolved by unit mass of the substance in changing under the same conditions from the liquid to the solid state.

The latent of fusion .of a substance is, therefore, defined as *the quantity of heat absorbed by unit mass of the substance in changing from the solid state to the liquid state, at the melting point of the substance.* It is also the quantity of heat evolved by unit mass of the substance in changing from the liquid state to the solid state at the freezing point of the substance.

It should be noticed, however, that the heat is "latent" in the liquid substance (as molecular potential energy), and it is therefore usual to associate the term "latent heat" with the process of *fusion*, or with the liquid form of the substance, and not with the process of solidification nor with the solid form of the substance. Thus, in the case of water substance, we speak only of the *latent heat of fusion of ice* or the *latent heat of water*.

The latent heat of fusion of any substance is thus a definite constant quantity of heat for a given unit of mass, and it will be seen that if this unit of mass is the same as that involved in the unit of heat, the number measuring the latent heat will be independent of the unit of mass selected. Thus, if the latent heat of a substance is L *gramme*-degrees per *gramme*, it is also L *kilogramme*-degrees per *kilogramme* or L *pound*-degrees per *pound*.

If the latent heat of fusion of any substance be L units of heat, then the quantity of heat absorbed by m units of mass in changing from the solid state to the liquid state at the melting

point of the substance is m L units. This is also the quantity evolved by m units of mass in changing from the liquid state to the solid state at the same temperature.

The general method of determining the latent heat of fusion of any substance cannot be dealt with here. The latent heat of fusion of ice, or the latent heat of water, can, however, be determined with fair accuracy by the method of mixtures as described below.

Experiment 48.—The determination of the *latent heat of fusion of ice*, or the *latent heat of water*, may be made by the following method.

Set up a water calorimeter ready for use, and let the temperature of the water in it be about 25° C.

In determining the mass of water in the calorimeter the weight of the vessel with the water in it should be noted more exactly than is usually necessary. The weighing should be made to the nearest centigramme at least.

Break up some ice into small pieces about the size of a nut, and wash the pieces well in clean water. Then select a number of pieces of suitable size, and after drying each piece carefully with filter paper drop it into the water in the calorimeter.

Stir the water as the ice is added, and when the temperature falls to about 10° C., stop adding ice, but continue stirring until all the ice is melted, and note the lowest temperature reached.

It is well, in this experiment, to have the stirrer made so that it can be used to keep the ice below the surface of the water in the calorimeter while melting.

When the final temperature is noted weigh the calorimeter vessel and its contents in order that the weight of the ice added may be found from the increase in the weight of the calorimeter. This weighing should also be made to the nearest centigramme.

In the weighings of an experiment of this kind it is generally most convenient to keep the stirrer in the calorimeter but to remove the thermometer. Care should be taken, however, to avoid loss of water in removing the thermometer at the end of the experiment.

Numerical Example.—Let the data found in an experiment of this kind be as follows.

| Weight of calorimeter, | . | . | . | 72·6 grammes. |
| Weight of calorimeter and water, | | . | 212·63 | ,, |

Initial temperature of water in calori-
meter, ... 23·6° C.

Final temperature, ... 9·4° C.

Weight of calorimeter and water after
addition of ice, ... 235·71 grammes.

Water equivalent of calorimeter, . 5·2 ,,

Before reducing these data it should be noted that the ice melted in the calorimeter is first converted into water at 0° C., and the water so produced is then raised from 0° C. to the final temperature of the mixture.

From the data given the mass of water in the calorimeter may be taken as 140 grammes, and the water equivalent of the calorimeter is 5·2 grammes. The heat lost by the calorimeter during the experiment is, therefore,

$$(145·2 \times 14·2) \text{ calories.}$$

Also, the mass of ice melted is 23·08 grammes, so that if L denote the latent heat of fusion of ice, the heat expended in first melting the ice at 0° C., and then in raising the water produced from 0° C. to 9·4° C., is

$$(23·08 \text{ L} + 23·08 \times 9·4) \text{ calories.}$$

We, therefore, get

$$23·08 \text{ L} + 23·08 \times 9·4 = 145·2 \times 14·2 ;$$
or,
$$23·08 \text{ L} = 1844·9 ;$$
or,
$$\text{L} = 80 \text{ nearly.}$$

That is, the latent heat of fusion of ice is given by the experiment to be very nearly 80 calories.

It should be noted that the weight of the ice is given by the difference of two weighings of the calorimeter, and may not be determined with sufficient accuracy if these weighings are not correct to the nearest centigramme. In this case the weight of the ice is fairly large, and it would have been accurate enough for ordinary work to weigh to decigrammes.

A number of very careful determinations of the latent heat of fusion of ice at 0° C. have been made, and it has been found as a general result that its value is almost exactly 80 units. That is, 1 gramme of ice absorbs 80 units of heat in changing from

ice at 0° C. to water at 0° C., and, similarly, 1 gramme of water gives out 80 units of heat in changing from water at 0° C. to ice at 0° C.

The fact that the latent heat of water is thus a comparatively large quantity explains why ice and snow melt so slowly, and also why water freezes slowly during continued frost. If the latent heat of water were not high, the water on the earth's surface would freeze quickly and in great masses during frosty weather, and the melting of ice and snow during a thaw would be so rapid as to become a serious source of danger. The snow line would also be raised, and the distribution of perpetual snow and ice on the earth's surface would be greatly changed.

Table of Latent Heats of Fusion.

Ice,	80
Zinc,	28·1
Tin,	14·6
Lead,	5·4
Sulphur,	9·4
Mercury,	2·8
Nitrate of soda,	63·0
Nitrate of potash,	47·4
Paraffin wax,	35·1
Benzene,	30·9

46. **Influence of Pressure on the Melting Point.**— The melting point of a substance is found to depend on the pressure to which the substance is exposed. The fact that pressure must affect the melting point of a substance was first suggested on theoretical grounds by Professor James Thomson in 1818, and has since been established on a sound theoretical basis and confirmed by direct experiment.

It is found that increase of pressure *raises the melting point* of the substance if the substance *expands* in melting, and *lowers the melting point* if the substance *contracts* in melting.

Ice is a notable example of a substance which contracts in

melting, so that its melting point is lowered by increase of pressure. That is, the melting point of ice under a pressure of one atmosphere is 0° C., but at higher pressures the melting point falls below 0° C. by an amount which increases with the pressure. The rate at which the melting point is lowered by increase of pressure is however very small. It can be calculated that the melting point of ice is lowered by about ·0073° C. for an increase in pressure of one atmosphere. That is, the melting point of ice under a pressure of 138 atmospheres is about −1° C. This result has been confirmed by actual experiment.

It will be seen from what has been said that if ice at any temperature is subjected to a pressure sufficiently great *to lower its melting point below its actual temperature,* the ice will melt. Also when the pressure is removed the water produced will freeze again at the existing temperature and form ice as before. This process by which ice melts under great pressure and the water produced freezes again when the pressure is relieved is known as *regelation.*

Experiment 49.—Take two small blocks of ice, place two flat faces in contact, and press the blocks firmly together for a short time.

It will be found that the two blocks are firmly frozen together. The ice at the points of contact of the two faces melts under the pressure, and the film of water so produced freezes again when the pressure is removed, and so the two blocks become united.

The process of regelation supplies the explanation of a number of familiar effects. The " making " of a snowball by pressing the snow together with the hands is due to regelation under the pressure applied. When, however, the snow is at a temperature a little below 0° C. the pressure applied by the hands is not great enough to lower the melting point below the existing temperature, and the snow will not " make." It is found, too, that snow or broken pieces of ice may be moulded by great pressure into masses of clear continuous ice of any desired form. Thus, if broken ice is placed in a strong cylinder and subjected

to pressure by means of a screw piston at one end of the cylinder it may be forced through a hole in the other end as a continuous cylinder of transparent ice.

The balling of snow in horses' feet and the formation of the thin sheet of clear ice which marks the track of the wheels of a heavy cart over snow are caused in the same way.

The process of regelation plays an important part, too, in the formation and flow of glaciers. The formation and growth of a glacier is very largely due to the melting of the snow at the snow line under the great pressure caused by the weight of the superincumbent snow and the subsequent freezing of the water so produced. The continuous downward flow of a glacier is facilitated also by the fact that when the flow is obstructed at any point the pressure soon becomes sufficiently great at that point to melt the ice. Then when the pressure is relieved the water freezes and becomes solid ice as before.

The most striking experiment illustrative of regelation is that due to Dr. Bottomley. It is described below.

Experiment 50.—Get a long bar-shaped block of ice and support it horizontally across the gap between two supports. Take a piece of copper wire about twice the height of the block of ice from the floor in length, attach a heavy weight to each end, and adjust it across the block of ice so that the weights hang some distance above the floor.

It will be found that the wire gradually cuts its way into the block and ultimately passes right through it. The block, however, is not cut through ; the path of the wire is marked by a section of clear ice, but the block is as strong as at first, and shows no signs of weakness at this section.

The pressure of the wire causes the ice immediately below it to melt, and the water so produced escapes above the wire and freezes again to clear ice. The path of the wire through the ice is thus closed by the ice formed behind the wire as quickly as it is made by the melting of the ice in front of the wire. The latent heat absorbed by the ice below the wire in melting is supplied mainly by the heat evolved by the water above the wire in freezing. The transfer of heat takes place through the wire by conduction, so that the rate at which the wire cuts through the block must depend upon the thermal

conductivity of its material. The better the conductivity of the material the more quickly the wire cuts through; a copper wire therefore passes through the block more quickly than an iron wire, and a string of catgut or other bad conducting material would not pass through at all.

The effect of increase of pressure on the melting point of substance which expands on melting has also been studied experimentally, and is found to be in accord with theory. Bunsen, for example, found that the melting point of paraffin wax was raised from 46·3° C. at atmospheric pressure to 49·9° C. at a pressure of 100 atmospheres.

47. **Laws of Fusion.**—The general laws of fusion and solidification may now be summarised in the following terms.

(i.) A substance, under a given pressure, fuses or liquefies in changing from the solid to the liquid state at a fixed temperature, which is the same as that at which it freezes or solidifies in changing from the liquid to the solid state. This temperature is called the *melting point* of the solid, or the *freezing point* of the liquid substance, and during fusion or solidification the temperature of the whole mass of the substance (liquid and solid) remains constant at this point throughout the process.

(ii.) A substance absorbs a definite constant quantity of heat per unit mass during fusion, and evolves the same quantity per unit mass during solidification. This constant quantity of heat, absorbed during fusion and evolved during solidification, by unit mass of the substance, is the *latent heat of fusion* of the substance.

48. **Solution.**—When a solid dissolves in a liquid it undoubtedly changes from the solid state to the liquid state. The process of the change is, however, essentially different from the simple change by fusion at the melting point.

If solution is not accompanied by chemical action of any kind, the process is always accompanied by the absorption of a quantity of heat, which may be considered as the latent heat of

the change of state which the dissolved substance undergoes. This heat is absorbed from the solution itself, so that the simple solution of a solid in a liquid is always accompanied by a more or less pronounced fall of temperature. For example, the solution of a quantity of ammonium nitrate or sodium sulphate in water at the ordinary temperature lowers the temperature of the solution 10° or 12° below zero. For this reason the solution of one of these salts in water is used as a means of obtaining a freezing mixture.

When solution is accompanied by chemical action the heat effects attending the process will be the resultant of the effects of the change of state and the chemical action. The change of state always involves absorption of heat, while the chemical action generally results in evolution of heat; the final effect may, therefore, be an absorption of heat, or an evolution of heat according to the relative magnitude of the two individual effects. Thus a mixture of sulphuric acid and snow results in a rise or fall of temperature according to the proportions in which the substances are mixed.

Any mixture of substances which enter into solution with a sufficient absorption of heat to lower the temperature of the solution well below 0° C. is called a *freezing mixture*. Thus, a mixture of ammonium nitrate or sodium sulphate and water forms a convenient freezing mixture during the solution of the salt. A more effective mixture is obtained by mixing pounded ice, or snow, and salt. In this case the ice and salt both change state, and the absorption of heat is sufficient to lower the temperature of the mixture to − 22° C. A mixture giving an even lower temperature is one of calcium chloride and snow; a mixture of four parts of the chloride with three parts of snow may fall as low as − 50° C. in temperature.

It will be understood that a freezing mixture is effective as a cooling agent only during the time in which the absorption of heat attending change of state is taking place in the mixture.

49. **Surfusion.**—A liquid with a definite freezing point—that is, one which crystallises in freezing—may, under certain conditions, be cooled many degrees below its freezing point without freezing. Thus, water in a capillary tube, or suspended as drops in a liquid of the same density, has been cooled as low as − 20° C. without freezing.

When a liquid is cooled in this way below its freezing point, the introduction of a small crystal of the solid substance causes freezing to begin at once, and the process is then continued with evolution of heat (the latent heat of fusion) until the temperature rises to the normal melting point of the substance. Any sudden disturbance of the liquid, or a slight mechanical jar during this abnormal cooling, generally has the same effect.

The physical state of the liquid when cooled below its normal freezing point is, in fact, an unstable one, and any slight disturbance at once precipitates the change from the liquid to the solid state.

Experiment 51.—Melt a quantity of sodium hyposulphite in a flask, and after closing the flask with a plug of cotton wool set it aside to cool.

It will be found that although the freezing point of the salt is about 47° C. it will, if undisturbed, cool to the ordinary temperature without freezing.

If the plug is now removed (very gently), and a crystal of the salt is dropped into the liquid, it at once freezes into a solid mass, and the evolution of heat which accompanies the change is sufficient to cause an appreciable rise of temperature.

50. **Ice Calorimeters.**—It will be seen that if the latent heat of fusion of ice is accurately known a quantity of heat may be measured by determining the mass of ice which it is able to melt. A calorimeter designed for the measurement of heat on this principle is called an **ice calorimeter.**

The simplest form of ice calorimeter is that originally used by Black for the determination of specific heat. It consisted

(as shown in Fig. 51) of a rectangular block of pure ice, in which a cup-shaped cavity was hollowed out at the centre of one of its faces. A slab of ice was also provided which fitted over this face and served as a cover for the cavity.

In this way the cavity, when covered, was enclosed by a continuous wall of ice at 0° C. No heat from without could enter the closed cavity, and the heat given out by any body placed within it could not pass out but would be wholly spent in melting the ice.

The general method adopted by Black for the determination of the specific heat of a substance with this calorimeter was comparatively simple.

Fig. 51.

The cavity in the block was first carefully dried with blotting-paper or a sponge.

A known mass of the substance heated to a known temperature was then dropped into the cavity, and the covering slab of ice was at once put on. The heated mass within the cavity will now cool to 0° C., and in doing so will melt a definite mass of ice. The water thus produced must evidently remain unchanged and quite constant in quantity so long as the walls of the cavity remain intact. After some time the cover was taken off, and the whole of the water in the cavity was carefully collected with blotting-paper and a sponge, and weighed. This gave the mass of ice melted by the heated mass placed in the cavity in cooling from a known temperature to 0° C. From

the data thus obtained the specific heat of the substance was calculated.

Numerical Example.—In an experiment with Black's ice-calorimeter a mass of 200 grammes of iron at 100° C. was placed in the cavity, and the mass of water melted by the iron was found to be 28·3 grammes.

The specific heat of iron may be calculated from the data of this experiment in the following way. Taking the latent heat of fusion of ice to be 80 units, the heat absorbed by 28·3 grammes of ice at 0° C., in changing to water at 0° C. is

$$(28\cdot3 \times 80) \text{ units.}$$

Also, if s denotes the specific heat of iron, the heat given out by 200 grammes of iron in cooling from 100° C. to 0° C. is

$$(200 \times 100 \times s) \text{ units.}$$

We, therefore, have

$$200 \times 100 \times s = 28\cdot3 \times 80,$$

or
$$s = \frac{28\cdot3 \times 80}{200 \times 100} = \cdot1132.$$

That is, the specific heat of iron is given by the experiment to be about ·113.

The principle of Black's calorimeter is thus quite simple and satisfactory, but it is evident that the method adopted in practice for determining the mass of ice melted is liable to serious error. It is possible, however, to use comparatively large masses of the substance and thus, by increasing the mass of ice melted, to diminish the percentage error made in its determination.

A modification of Black's calorimeter, devised by Laplace and Lavoisier, is shown in Fig. 52. The ice melted in the inner layer by the heated substance placed in the central chamber is determined by running off the water at the side tap shown in the figure and weighing it.
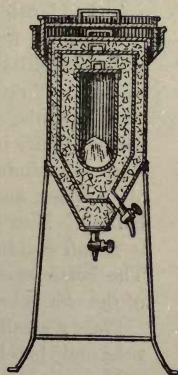
Fig. 52.

Although this instrument gave fairly good results in the hands of Laplace and Lavoisier, it is open to the same objection as Black's simpler form, and is quite useless for accurate work.

The only form of ice calorimeter capable of accurate work is that invented by Bunsen in 1871. Instead of attempting to determine the mass of ice melted in the calorimeter by collecting it and weighing it, Bunsen devised a means of measuring with great accuracy the decrease in volume which takes place when the ice melts and becomes water at 0° C.

It has already been noticed that when one gramme of ice changes from ice at 0° C. to water at 0° C. the decrease in volume is about 0·091 c.c., or about one-eleventh of a cubic-centimetre. It follows, therefore, that a change in volume of 1 c.c. may be taken to indicate the melting of 11 grammes of ice or the evolution of (11 × 80) or 880 units of heat.

The principle of Bunsen's ice calorimeter is illustrated by the following experiment.

Experiment 52.—Find the Specific Heat of Silver with the simple form of Bunsen's Ice Calorimeter described below.—Get a wide-mouthed bottle and fit it with a good rubber stopper. Then fit through the stopper a small stout-walled test-tube and a length of thick-walled capillary tube, about 1 mm. bore, in the manner shown in Fig. 53. First find the capacity of unit length of the bore of the capillary tube and record the result. Then fill the bottle with small pieces of pure ice and water at 0° C., and insert the stopper and tubes so as to exclude every trace of air. The ice should be quite free from air bubbles, and the water should have been freed from air by long boiling. Now place the bottle inside a large beaker or jar and pack it round carefully with small pieces of ice as shown in the figure. The bottle should be completely surrounded with ice, but the mouth of the test-tube should appear well above the surface of the packing.

Place a small pad of fine copper gauze at the bottom of the test-tube and then half fill the tube with water.

Now allow this apparatus to stand for some time (preferably in ice in a larger vessel) until the level of the water in the capillary tube is practically constant. When this state is attained, bring the level near the upper end of the tube by forcing the tube a little deeper into the bottle. Then when the level is quite steady near this end note

its position, either by means of a scale provided for the purpose or by measuring its distance in mms. from the open end of the tube.

Now heat about 20 grammes of silver in a heater to 100° C. and then drop it into the test-tube. The heat given out by the silver in cooling to 0° C. will melt some of the ice in the bottle, and the consequent decrease in the volume of the contents of the bottle will be indicated by a fall of the level of the water in the capillary tube.

Note the point at which the level again becomes steady when the melting caused by the heat given out by the silver is complete. The capacity of the bore of the tube between the two points at which the level of the water was steady before and after dropping the silver into the test-tube evidently gives the decrease in volume corresponding to the amount of ice melted in the bottle ; and the capacity of the bore per unit length being known, this decrease in volume can be at once determined. The specific heat of the silver can then be calculated in the manner indicated below.

Numerical Example. — Thus, in an apparatus of this kind let the capacity of unit length of the bore of the tube be ·008 c.c., and let the level of the water column in the capillary tube be observed to fall a distance of 81 mms., when 10 grammes of silver heated to 100° C. is dropped into the test-tube and allowed to cool there to 0° C.

Fig. 53.

Here the quantity of ice melted is evidently such as to cause a decrease of volume of (8·1 × ·008) c.c., or ·648 c.c. in changing from ice at 0° C. to water at 0° C.

Now, as explained above, a decrease in volume of 1 c.c. indicates the melting of 11 grammes of ice and the evolution of (11 × 80) or 880 units of heat. A decrease of ·648 c.c., therefore, indicates the evolution of (·648 × 880) units of heat.

This heat, however, was evolved by 10 grammes of silver in cooling from 100° C. to 0° C. Hence, if s denote the specific heat of silver we have

$$10 \times 100 \times s = ·648 \times 880 ;$$

or,

$$s = \frac{·648 \times 880}{1,000} = ·057.$$
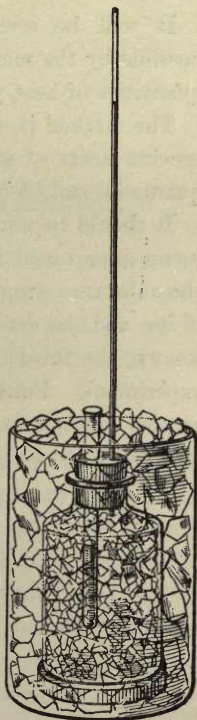
That is, the specific heat of silver is given by the experiment to be about ·057.

It will be seen from the example just given that it is possible by the method of Bunsen's calorimeter to measure small quantities of heat with great accuracy.

The method is, therefore, specially suitable for determining the specific heats of substances, of which only comparatively small quantities can be obtained for experiment.

It should be noted that the reduction of the data of the foregoing experiment involves three quantities—the specific heat of the substance dropped into the test tube, the latent heat of fusion of ice, and the density of ice. If any two of these quantities are known, the third can evidently be found from the data of the experiment. Bunsen determined the latent heat of fusion of ice by this method to be 80·03 units; he also found the density of ice at 0° C. to be ·9167 gramme per cubic centimetre.

CHAPTER IX.

VAPORISATION AND CONDENSATION.

51. Vaporisation and Condensation.—The process by which a substance changes from the liquid state to the state of vapour is called **vaporisation,** and the reverse process by which a substance changes from the vapour state to the liquid state is called **condensation.**

It will be found that, in general, the phenomena of vaporisation and condensation are exactly analogous to those of fusion and solidification. There is, however, one important difference between these two cases of change of state. A solid changes to a liquid only at its melting point, and the solid and liquid forms of the substance can co-exist in equilibrium * only at this temperature. A liquid, on the other hand, gives off vapour at all temperatures, and a liquid and its vapour may be in equilibrium * at any temperature at which they can co-exist.

This important difference between a solid and a liquid is evidently due to the difference in the aggregation of the molecules of the substance in the two states. Although the molecules in a solid are separate from each other and free to vibrate, they are fixed in position and cannot move about from

* A solid and a liquid, or a liquid and its vapour, are said to be in equilibrium when the two forms of the substance exist in contact with each other without there being any tendency for one form to change into the other. Thus, ice and water at 0° C. may exist together for any length of time in an enclosure at 0° C. without there being any change in the relative quantities of ice and water present in the mixture. That is, the ice does not melt nor the water freeze.

point to point in the substance. The molecules of a liquid, on the other hand, move about freely in the substance, and it is, therefore, possible for molecules at the free surface of the liquid to escape into the adjoining medium. These molecules which escape at the surface constitute the vapour of the liquid, and as the escape may take place at any temperature, a liquid is found to give off vapour at all temperatures.*

The process of vaporisation and condensation is further complicated by the fact that a vapour, like a gas, exerts pressure, and vapour pressure, therefore, becomes a factor to be considered in the study of the process.

The experimental study of vaporisation and condensation involve, therefore, not only the determination of the temperature effects, the volume effects, and the heat effects which accompany the change, but also the investigation of the influence of vapour pressure on this change of state.

The vaporisation of a liquid when heated, and the condensation of the vapour when cooled, is illustrated by the following experiment.

Experiment 53.—Set up the apparatus shown in Fig. 54.

The flask is a distillation flask provided with a side delivery tube and fitted with a thermometer. An ordinary flask fitted with a cork carrying the thermometer, and a bent delivery tube, would serve the purpose equally well.

The flask is connected by a rubber connection to the double tube *condenser* shown in the figure. This condenser consists, as shown, of an inner tube surrounded by a wider tube provided with side inlet and outlet tubes. The inner tube can thus be jacketed with cold water by passing a current of water from a tap through the outer tube. The current of water should enter from the tap by the *lower* side tube, and pass on to the sink by the upper tube.

Place a quantity of water in the flask, and heat it to boiling.

It will be seen that the vapour from the boiling water condenses to

---

* Experiment shows that a solid may also give off vapour, and that this vapour may exert an appreciable pressure at temperatures near the melting point of the solid. See also Art. 60 on Sublimation.

water in the inner tube of the condenser, where it is cooled by the current of cold water maintained through the outer tube, and drops from the end of the tube into the beaker or flask placed to receive it.

The double process of vaporisation and condensation effected as in the foregoing experiment by means of a condenser is called **distillation**. The process is frequently used as a means of obtaining pure *distilled* water from water containing impurities in solution.
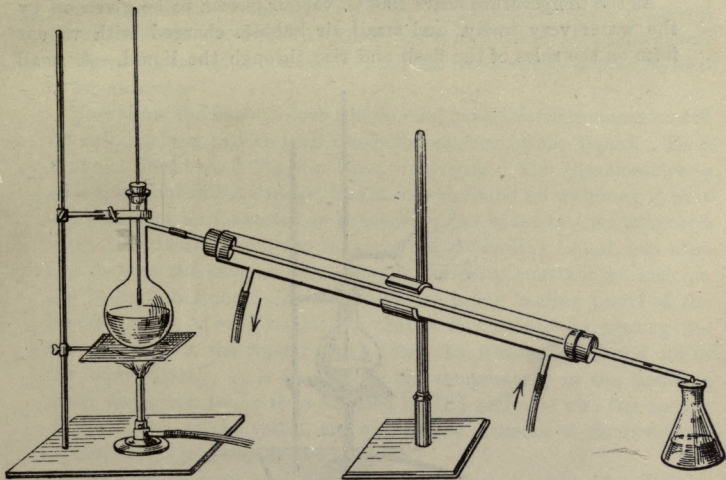
Fig. 54.

52. **The Boiling Point of a Liquid.**—The process of change of state from the liquid state to the vapour state by *boiling* is, in the case of water, a very familiar one. The general nature of the process and the temperature effects with which it is accompanied, may be studied by the method of the following experiment.

Experiment 54.—Fit a flask with a thermometer and a delivery tube as shown in Fig. 55. Half fill the flask with water and adjust the thermometer in the cork so that its bulb and some part of the stem is immersed in the water.

Now heat the flask gently with a Bunsen and note what takes place as the temperature rises.

It will be seen as the heating proceeds that vapour is given off from the surface of the liquid and condenses in the neck and on the sides of the flask.

As the temperature rises vapour appears to be given off more and more freely, and ultimately begins to escape by the delivery tube into the air, where it becomes visible by condensing into a slight cloud or mist of very minute drops of water.

As the temperature nears 100° C. vapour is seen to be given off by the water very freely, and small air bubbles charged with vapour form on the sides of the flask and rise through the liquid. A small
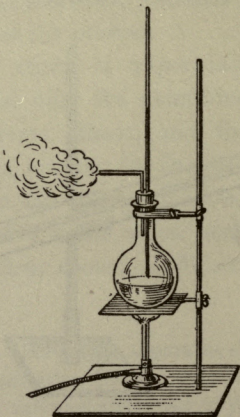
Fig. 55.

cloud of condensed vapour will be seen to form at the mouth of the delivery tube, where the escaping vapour mixes with the colder air. It will be noticed, however, that the vapour inside the flask and in the delivery tube is itself quite invisible; and for a short distance, too, beyond the mouth of the delivery tube the vapour is invisible, but as it mixes with the colder air the cloud of minute water particles formed by its condensation is clearly seen and is often supposed to be the vapour itself.

When the temperature rises to 100° C. it will be seen that bubbles of vapour form and escape so rapidly at the surface that the liquid is somewhat violently disturbed and agitated, and is said to *boil* or to enter into *ebullition*. During this state of ebullition water vapour

is given off continuously, and the cloud of condensed vapour at the mouth of the delivery tube becomes more marked. It should be noticed, however, that this cloud is formed only in the region where the vapour first meets the colder air, and does not increase in size beyond a comparatively small limit ; it is dissipated at its outer boundary by vaporisation and diffusion into the surrounding air as quickly as it is formed, and so remains after reaching a certain limit of constant extent.

As the liquid continues to boil it will be seen that the temperature remains practically constant at 100° C. Careful observation will show that the temperature varies slightly through a range of perhaps half a degree above and below 100° C., but on the average it may be said to be constant.

Now allow the flask to cool a little, and raise the thermometer until its bulb is about half an inch above the surface of the liquid. Then heat the liquid until it again boils vigorously. The thermometer is now immersed in the *vapour*, and it will be found on watching it that the temperature indicated is practically the same as that indicated when the thermometer was immersed in the boiling liquid, but that in this case the temperature remains perfectly constant as long as the boiling continues. This temperature is the boiling point of the liquid ; and it should be noticed that it is obtained by placing the thermometer in the vapour rising from the boiling liquid and not in the liquid itself. It is found that the temperature of the liquid is never quite constant ; it is affected by the material and the nature of the surface of the vessel, and also by the presence of dissolved air or small solid particles in the liquid.

If the experiment here described is repeated with other liquids such as alcohol, aniline, and ether, it will be found that precisely the same general results are obtained, but that a different boiling point is obtained for each liquid.

It will be seen from this experiment that while a liquid gives off vapour at all temperatures, it changes completely from liquid to vapour by the process of **boiling** or **ebullition** at a definite temperature which is constant throughout the process. This temperature is called **the boiling point** of the liquid, and is, under given conditions, a distinctive characteristic of the liquid.

The boiling point of a liquid is obviously the *highest temperature* at which the liquid can, under the given conditions,

exist as a liquid. The temperature cannot be raised above this point without converting the whole mass of the liquid into vapour.

It should be noticed that the boiling point is determined, as explained above, by placing the thermometer in the vapour rising from the boiling liquid, and not in the liquid itself.

> **Experiment 55.**—Fit up a flask with a thermometer and delivery tube as in Exp. 54 ; half fill it with water, and adjust the thermometer so that the bulb and the lower part of the stem are immersed in the water.
>
> Now heat the water to boiling and let it boil for some time. It will be seen that as the water loses the air dissolved in it by continual boiling, it appears to boil less freely and evenly ; the vapour is given off in occasional sudden bursts, and not in a steady stream of bubbles as at first. At the same time the temperature rises and falls in a correspondingly irregular way ; in the period of comparative quiet before one of the sudden bursts of vapour the temperature rises, but falls at once when the burst takes place.
>
> If the boiling is still continued the spasmodic character of the process becomes more and more marked, and the vapour is given off in short explosive bursts, followed by periods of comparative quiescence. At the same time the range through which the temperature of the liquid rises and falls increases, and may extend to several degrees. This peculiarity of the process of boiling is known as *bumping*, and some liquids, such as sulphuric acid, can boil only in this way. The same causes which lead to bumping may, under certain conditions, give rise to dangerous explosions. When the water begins to bump remove the cork, and put a few coarse particles of sand into the flask. It will now be seen that the water boils easily and steadily for some time. A steady stream of vapour bubbles is given off from each of the sand particles, which appear to serve as centres for the formation of the bubbles.
>
> After some time, however, bumping will again set in.
>
> A number of pieces of broken glass or pieces of platinum foil will be found more effective than the grains of sand in promoting steady continuous boiling, but the best means to adopt for this purpose is to add a few pieces of some porous substance, such as pumice stone, brick, or charcoal to the water.
>
> Although the temperature of the boiling liquid may thus vary considerably, the temperature of the vapour under given conditions is found to be perfectly constant.

The boiling point of a liquid is usually determined by the method indicated in Exp. 54, and explained more fully below.

> **Experiment 56.—Determine the Boiling Point of the Given Liquid.**—Fit up a small flask as in Fig. 55, and fill it about one-third full with the liquid. Add a few pieces of broken glass to promote easy boiling, and adjust the thermometer in the cork so that the bulb and as much of the stem as possible are immersed in the vapour. The lower end of the bulb should, however, be well clear of the spray which rises from the surface of the boiling liquid. It may be necessary at a later stage in the experiment to re-adjust the thermometer in order that the boiling point may be read conveniently.
>
> Heat the liquid to boiling, and note the constant temperature at which it boils. This temperature is the boiling point.
>
> Instead of fitting the flask with a bent delivery tube as shown in Fig. 55, it is generally more satisfactory to fit a long straight piece of fairly wide tubing in its place. In the case of most liquids the vapour will condense in this tube without the addition of a condenser, and the condensed liquid will run back into the flask. In this way the vapour does not escape into the air, and the liquid is not wasted.
>
> In some cases, however, it is necessary to fit the tube with a water condenser in the manner shown in Fig. 56.

It will be found later that the boiling point of a liquid depends upon the pressure under which it boils. The normal boiling point of a liquid is the temperature at which it boils under the normal atmospheric pressure.

Fig. 56.

53. Vapour Pressure.

—The fact that the vapour of a liquid at any given temperature exerts a pressure is shown by the following experiment.

> **Experiment 57.**—Fit up a simple barometer in the usual way, and then pass a small quantity of water or alcohol up the barometer tube into the vacuum space above the mercury column. This may be done conveniently by means of a small pipette with a bent point.
>
> It will be seen that when the liquid reaches the vacuum some of it
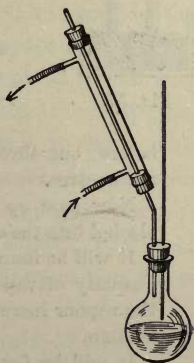
immediately vaporises, and the pressure of the vapour which fills the space will be sufficient to depress the mercury column several centimetres. The distance through which the column is depressed evidently measures the pressure exerted by the vapour. Fig. 57 shows two simple barometer tubes. In one, A, the vacuum is perfect; in the other, B, a small quantity of liquid has been introduced into the vacuum. The difference between the heights of the two mercury columns measures the pressure of the vapour in B.
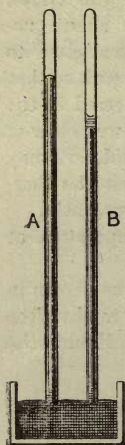
The manner in which the magnitude of the pressure exerted by the vapour in the vacuum space of the barometer tube depends upon the quantity of vapour present in the space as indicated in the following experiment.

Fig. 57.

Experiment 58.—Fit up a simple barometer tube as in the foregoing experiment. Dip a small piece of filter paper in alcohol and pass it up into the vacuum space of the tube.

It will be seen that the mercury is depressed as before, but through a much shorter distance—perhaps only a few millimetres.

Now pass up several small pieces of filter paper moistened with alcohol into the vacuum one after the other, and note what takes place.

It will be found that as the alcohol on each piece vaporises and the quantity of vapour in the space increases, the pressure exerted by the vapour increases, and causes a further depression of the mercury column.

It will be found, however, that the pressure cannot be increased indefinitely in this way, not even by passing a quantity of liquid up into the space. The pressure exerted by the vapour quickly reaches a *maximum value*, and when this value is reached it will be found that any liquid present in the space remains unvaporised.

If the experiment is repeated several times with the same liquid at the same temperature, it will be found that the *maximum pressure* exerted by the vapour is always the same.

If the experiment is tried with different liquids at the same temperature it will be found that the *maximum vapour pressure*, although constant at a given temperature for a given liquid, is different for different liquids at the same temperature.

It will be seen from this experiment that when a liquid vaporises in a limited space, at a given temperature, the vapour exerts a pressure which attains a definite *maximum value* when vaporisation ceases, and the liquid and vapour are in equilibrium.* The vapour is then at its *maximum density*, and the space is said to be *saturated* with the vapour. A vapour in equilibrium with its liquid and at its maximum pressure and density is generally called a **saturated vapour.** †

A saturated vapour, being already at its maximum pressure and density, cannot be subjected to an increase of pressure or compressed. If an attempt is made to compress it the only result is to produce condensation of the vapour in the same proportion as the volume is decreased. Thus, if the barometer tube B, in Fig. 57, is lowered in the cistern, the height of the mercury column remains quite unchanged, but the vapour in the vacuum space condenses as the volume of the space is reduced.

If the volume occupied by a saturated vapour *in contact with its liquid* is increased, vaporisation from the liquid at once begins, and the increased volume is quickly saturated or filled with saturated vapour. If, however, a saturated vapour, apart from its liquid, is free to expand, it expands and becomes an *unsaturated vapour*. In this state it conforms to Boyle's Law and Charles' Law with an exactness which depends upon how far it is removed from saturation.

In the experiments described above the liquid is allowed to vaporise *in a vacuum*. It is found, however, that exactly the

---

* It should be noticed that the equilibrium is dynamical in character. There is a continuous interchange of molecules between the liquid and the vapour at the surface of contact, and at this stage of the process the same number of molecules pass in a given time from the vapour to the liquid as from the liquid to the vapour.

† It is helpful to remember that the phrases, "a vapour *in equilibrium with its liquid*," "a vapour at its *maximum pressure*," "a vapour at its *maximum density*," and "a *saturated vapour*," all apply to the same state of the vapour at any given temperature.

same general results are obtained when the liquid vaporises in air, or in any similar medium. The liquid vaporises much more quickly in a vacuum, but the pressure exerted by the vapour is not affected by the presence of air or any other gaseous medium which has no chemical action on the vapour.

These facts are conveniently illustrated by the method of the following experiment.

Experiment 59.—Fit the lower part of a siphon barometer, B, and a dropping funnel, F, into a large flask or jar in the manner shown in Fig. 58. The fitting is readily managed by using a split cork, and then sealing the mouth of the flask with melted wax.
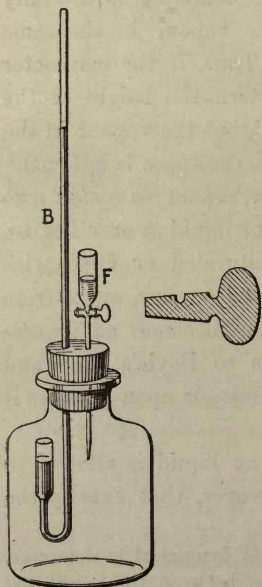
Fig. 58.

The stopcock of the funnel should be constructed as shown in the figure ; the barrel is not pierced through in the usual way, but is provided instead with a small cup-like depression as shown in the figure. When the stop-cock is adjusted so that this cup is on the upper side, it fills with the liquid in the funnel, and then when the stopcock is turned down this small quantity of liquid falls into the flask. In this way it is easy to transfer successive small quantities of the liquid from the funnel to the flask.

When the apparatus is set up, place some alcohol in the funnel, and note carefully the difference of the mercury columns of the siphon barometer.

Now transfer a drop of alcohol from the funnel to the flask, and note the result. It will be found that in a few minutes the pressure indicated by the barometer—that is, *the pressure inside the flask*, shows a small increase.

Continue to add drop after drop in this way, and note the result produced by the introduction of each drop.

It will be found that the pressure due to the vaporisation of the liquid in the flask increases *slowly* after the introduction of each drop of liquid, and that ultimately the drops remain unvaporised at the

bottom of the flask, and the increase in pressure in the flask due to the vapour present in it attains a maximum value. It will be found, too, that this maximum value is exactly the same as that obtained at the same temperature by the method of Exp. 57.

It may be noticed that the experiment illustrates a special case of a general law relating to the pressure exerted by a mixture of gases. This law, first formulated by Dalton, and known as **Dalton's Law**, states that in a space occupied by a mixture of gases which show no chemical interaction, each constituent exerts exactly the same pressure as if it alone occupied the space, and the pressure exerted by the mixture is the sum of the pressures of the individual constituents. That is, in the case here considered, the pressure exerted by the vapour in the flask is the same as if it alone filled the flask, and the pressure of the mixture of air and vapour in the flask is the sum of the pressures exerted individually by the air and the vapour.

It has now been established that the vapour given off by a liquid at any temperature exerts a pressure, and that this pressure attains a maximum value which is constant at any given temperature. It now remains to consider how the maximum vapour pressure of any substance depends upon the temperature. The relation between maximum vapour pressure and temperature for any liquid may be determined by the method indicated in the following experiment.

Experiment 60.—Set up a simple barometer as in Exp. 57, and fit a wide jacket tube over the barometer tube in the manner shown in Fig. 59. If the barometer tube has no scale engraved on it, arrange a millimetre scale near the tube, so that the height of the mercury column can be accurately read on it.

When the barometer is set up note the position of the top of the column on the scale.

Then pass a small quantity of water up into the vacuum of the barometer tube, and notice the comparatively small depression of the mercury column produced by the maximum pressure of the water vapour at the ordinary temperature.

Now pour some warm water at about 50° C. into the jacket tube surrounding the barometer tube, and note the general result.

It will be found that more of the liquid in the barometer tube is rapidly vaporised, and that the pressure exerted by the vapour very quickly rises to a much higher value.

When these general observations have been made, suspend a thermometer in the water in the jacket tube so that it hangs near the column of vapour in the barometer tube, and provide a suitable stirrer for the water jacket.

Then allow the water in the jacket tube to cool slowly and note the position of the top of the mercury column on the scale at intervals of five or ten degrees as the temperature falls from 50° C. to the ordinary temperature. By adding ice to the water jacket readings may be taken in this way down to 0° C. The water in the jacket tube should be stirred almost continuously during the cooling in order to make sure that the temperature given by the thermometer is the temperature of the vapour in the inner tube.

The maximum pressure of water vapour at the observed temperature can now be determined from the readings taken at these temperatures ; the depression of the mercury column below the level first noted gives the maximum vapour pressure at each temperature.

It will be found that the maximum vapour pressure increases rapidly as the temperature increases, and that equal increments of temperature produce *increasing* increments of pressure. In the case of water vapour, for example, the following results should be obtained between 0° C. and 50° C. : —

Temperature.	Maximum vapour pressure.
0° C.	4·6 mm.
10° C.	9·2 ,,
20° C.	17·4 ,,
30° C.	31·5 ,,
40° C.	54·9 ,,
50° C.	92·0 ,,

If now we wish to extend our observation to higher temperatures we may heat the water in the jacket tube by passing steam into it, and take observations as the temperature rises, or we may repeat the experiment in the form here described, beginning the observations at a much higher temperature.

It will be found, however, that when the temperature rises above 60° C. or 70° C. the column of vapour becomes so long that it is necessary to extend the jacket tube to the full length of the barometer

tube, and it is practically impossible to maintain this long column at anything like a uniform temperature throughout its length.

The method of this experiment is, therefore, unsuitable when the vapour pressure is greater from 15 cms. to 20 cms. at most.

If the experiment is repeated for any other liquid exactly the same general results will be obtained, but the value of the maximum vapour pressure at any given temperature will, of course, be different for different liquids.

Experiment 61.—When the vapour pressure exceeds the limit suitable for the apparatus of the foregoing experiment, the method here described may be adopted.

Fit up a *siphon* barometer, and place a quantity of the liquid whose vapour pressure is to be measured on the surface of the mercury in the *lower open limb* of the tube. This limb, for the purpose of this experiment, should be longer and wider than usual, and should be drawn out at its upper end to a point so that it can, when necessary, be easily sealed.

Now boil the liquid in the tube until all air is expelled by the vapour of the liquid, then seal the tube.

The pressure of the vapour in the limb will now be given directly by the difference in the heights of the mercury columns in the tube.

Now immerse the lower limb of the barometer tube in a water or oil bath, as shown in Fig. 60. Then heat the bath gently and take readings of the maximum vapour pressure every five or ten degrees as the temperature rises.

It will be found, exactly as in the foregoing experiment, that the maximum vapour pressure increases as the temperature rises, and that the increments of pressure corresponding to equal increments of temperature increase very rapidly.

In this experiment the behaviour of the liquid as it approaches its normal boiling point is of special interest.

It is found, in the case of every liquid, that as the temperature approaches the normal boiling point of the liquid the maximum vapour pressure approaches the normal atmospheric pressure, and that at the boiling point the maximum vapour pressure is exactly equal to the normal atmospheric pressure. That is, in this experiment it will be found that when the temperature of the bath reaches the normal boiling point of the liquid in the tube, the difference in height of the two mercury columns will be equal to the height of the barometer. Further, if the temperature be raised above the boiling point the maximum vapour pressure increases, and the liquid is in equilibrium with its vapour under the increased pressure.

That is, the liquid and its vapour at the boiling point and above it (as far as our present observations go), behave exactly as they do at temperatures below the boiling point. The main point to be noticed is that the maximum vapour pressure at the normal boiling point is the normal atmospheric pressure.

These experiments show that the maximum vapour pressure of a liquid increases as the temperature increases. As the
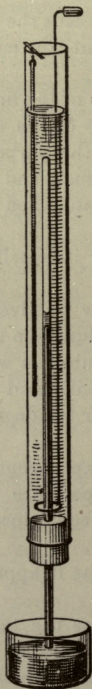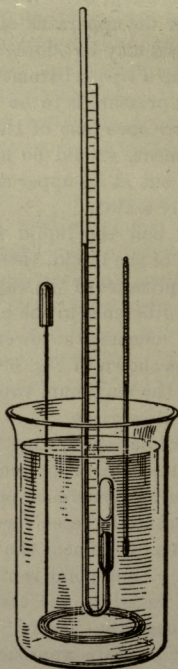
Fig. 59.   Fig. 60.

temperature rises to the boiling point of the liquid, the vapour pressure increases through values less than one atmosphere to the normal atmospheric pressure; at the boiling point the vapour pressure is exactly equal to the normal atmospheric

pressure ; and, as the temperature rises above the boiling point, the vapour pressure increases through values greater than one atmosphere. How far this increase of vapour pressure with rise of temperature goes on is a matter for further experiment, and cannot be considered here.

Regnault made a very careful determination of the maximum vapour pressure of water vapour through a wide range of temperature. A few of the results he obtained between 0° C. and 200° C. are given below.

MAXIMUM PRESSURE OF WATER VAPOUR (*Regnault*).

Temperature (° C.).	Pressure (mm.).	Temperature (° C.).	Pressure (mm.).
0	4·6	90	525·5
10	9·2	100	760·0
20	17·4	110	1,075·4
30	31·5	120	1,491·3
40	54·9	130	2,030·3
50	92·0	140	2,717·6
60	148·8	150	3,581·2
70	233·1	200	11,689·0
80	354·6		

Similar results have been obtained for many other liquids. It has not been found possible, however, to formulate the relation between maximum vapour pressure and temperature as a law, or to express it mathematically. The relation can, however, be expressed graphically by a smooth curve of characteristic form, so that by plotting a curve from data such as those given above for water vapour the maximum vapour pressure at any temperature within the range of the data can be found by interpolation. Fig. 61 shows the curve obtained by plotting Regnault's results for water vapour between 0° C. and 100° C.

Data for extending the curve below 0° C. may be obtained by measuring the maximum pressure of the vapour in contact with water when super-cooled below 0° C., as explained in Art. 28.

54. Influence of Pressure on the Boiling Point of a Liquid.—The results obtained in the foregoing article seem to indicate that a liquid boils when the maximum pressure of its vapour is equal to the external pressure under which it boils.

The main result on which this conclusion depends is further confirmed by the following experiments which show conclusively that the maximum vapour pressure at the boiling point of a liquid is equal to the external pressure at which it boils.
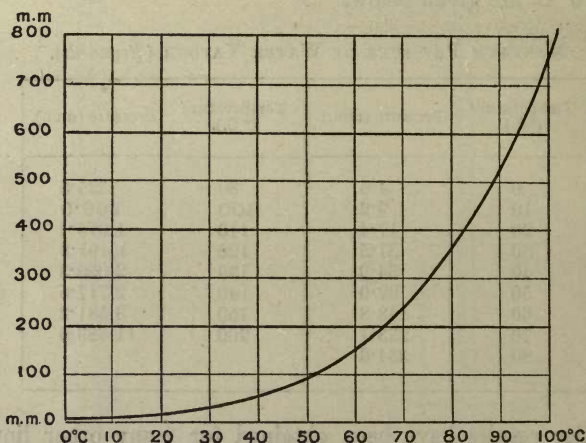
Fig. 61.

Experiment 62.—Fit the short limb of the siphon barometer described in Exp. 61 with a jacket tube as shown in Fig. 62. Place a quantity of any convenient liquid in the limb and seal it up, as explained in Exp. 61 ; then jacket this liquid and its vapour with vapour from *the same liquid,* boiling freely under the atmospheric pressure. It will be found then that the difference in the heights of the mercury columns in the barometer tube is exactly equal to the barometric height at the time of the experiment.

That is, the maximum pressure of the vapour in the short limb of the tube is exactly equal to the atmospheric pressure. The liquid in the tube is, however, the same as the liquid which is boiling under this pressure to supply the vapour jacket, and it is at the same temperature as this liquid. It follows, therefore, that the maximum

pressure of the vapour of the boiling liquid is exactly equal to the atmospheric pressure under which it boils.

Experiment 63.—Take a piece of glass tubing, close one end, and make a small U-shaped bend at the closed end. Fill the bend and the short closed limb completely with mercury, then pass a small quantity of any suitable liquid round the bend so that it floats to the top of the closed limb. Care must be taken to prevent air entering the tube with the liquid.
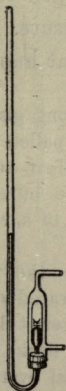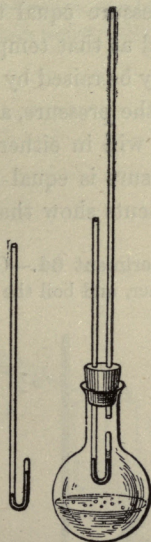
Fig. 62.   Fig. 63.

Now place a quantity of *the same liquid* in a flask and fit the tube into the flask, as shown in Fig. 63, so that the U-shaped bend is completely immersed in vapour when the liquid in the flask is boiled.

Now boil the liquid in the flask, and note that when the liquid boils freely the mercury stands *at the same level* in the two limbs of the U-tube. This shows that the pressure of the vapour in the closed limb is equal to the external atmospheric pressure. That is, the pressure of the vapour in the flask is equal to the external atmospheric pressure under which the liquid in the flask boils.

It may be noted here that this experiment indicates *a convenient method of finding the boiling point of a liquid* which is obtainable only in small quantities.

The liquid is introduced into the closed limb of the **U**-tube as in this experiment. It is then placed with a suitable thermometer in a water or oil bath, and the bath is heated until the mercury is at the same level in the two limbs of the tube. The temperature at which this occurs is evidently the boiling point of the liquid.

If this result is taken to be generally true, it follows that a liquid may be made to boil at any temperature by making the external pressure equal to the maximum pressure of the vapour of the liquid at that temperature. That is, the boiling point of a liquid may be raised by increasing the pressure and lowered by decreasing the pressure, and the temperature at which the boiling takes place will in either case be that at which the maximum vapour pressure is equal to the external pressure. The following experiments show that this is actually what happens.

Experiment 64.—Get a large flask of strong glass, half fill it with water, and boil the water until all air is expelled from the flask by the steam. Then cork the flask tightly, remove the burner and insert the flask on a ring of a retort stand, as shown in Fig. 64.
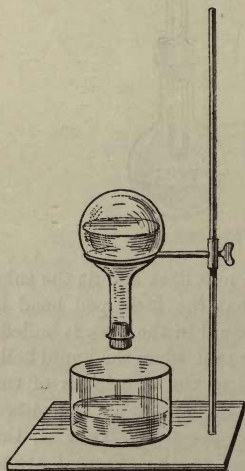
The space above the water is now occupied with saturated vapour in equilibrium with the water at the temperature existing inside the flask. If, however, cold water is poured over the flask the vapour condenses almost entirely, and the pressure in the space is very greatly reduced. The water is still warm, so that *its temperature is much above the boiling point under this greatly reduced pressure;* it therefore boils vigorously for a few seconds until the space is again filled with vapour and equilibrium re-established.

The liquid may be made to boil in this way repeatedly down to a comparatively low temperature.

Fig. 64.

This familiar experiment is due to Franklin, and is generally known as **Franklin's Experiment.**

Experiment 65.—Connect a small copper boiler, B, through a condenser, C, with an air reservoir, R, in which the pressure of the air may be increased or diminished by pumping air into it or out of it by means of a suitable air pump. A manometer, M, connected to the reservoir measures the pressure in the reservoir and boiler, and a thermometer fitted into the boiler gives the temperature of the vapour in the boiler.

It is evidently possible with this apparatus to adjust the pressure to which the liquid in the boiler is exposed to any desired value, greater or less than the atmospheric pressure, and then to determine the temperature at which the liquid boils under this pressure.
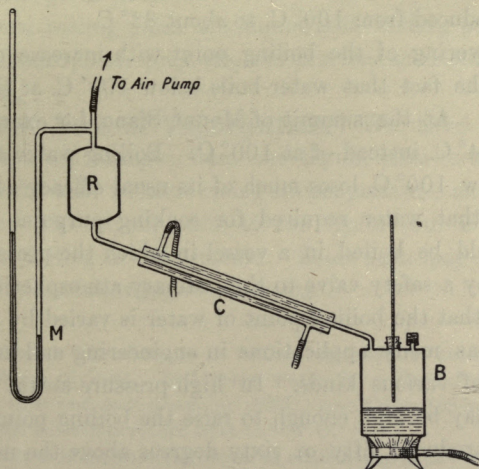
Fig. 65.

It will be found on doing this that the boiling point is raised by increasing the pressure, and lowered by decreasing the pressure, and that the boiling point under any pressure is the temperature at which the vapour pressure has the same value.

This apparatus was used by *Regnault* for the determination of the maximum pressure of water vapour. When boiling takes place at any temperature indicated by the thermometer the corresponding maximum vapour pressure is equal to the external pressure, and is, therefore, given by the manometer.

These experiments show that a liquid boils when its temperature reaches the point at which the maximum pressure of its

vapour is equal to the external pressure. The boiling point of a liquid may, therefore, be defined generally as the temperature at which the maximum pressure of the vapour of the liquid is equal to the external pressure at the surface of the liquid.

The magnitude of the effect of change of pressure on the boiling point of water is shown in the table given on p. 163. It will be seen, for example, that it is necessary practically to double the pressure in order to raise the boiling point of water from 100° C. to 120° C., and by halving the pressure the boiling point is reduced from 100° C. to about 82° C.

The lowering of the boiling point with increase of pressure explains the fact that water boils below 100° C. at the top of a mountain. At the summit of Mount Blanc, for example, water boils at 84° C. instead of at 100° C. Boiling water at temperatures below 100° C. loses much of its usual efficacy as a cooking agent, so that water required for cooking purposes at a high level should be boiled in a vessel in which the pressure can be adjusted by a safety valve to the ordinary atmospheric pressure. The fact that the boiling point of water is varied by increase of pressure has many applications in engineering and in industrial processes of various kinds. In high-pressure steam boilers the pressure may be high enough to raise the boiling point at which steam is produced, fifty or sixty degrees above the normal boiling point. Papin, who first discovered the fact that the boiling point of water is varied by increasing the pressure, invented a " digester " known as *Papin's Digester*, in which gelatine is extracted from bones by digesting them with water heated above 100° C. in a closed vessel * provided with a safety valve.

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* When water or any liquid is heated in a closed vessel the temperature of the water will evidently rise until the pressure of the vapour becomes great enough to open the safety valve, or to burst the vessel if there is no valve. When the valve opens, the water may be many degrees above 100° C., its boiling point under the reduced pressure in the vessel; the opening of the valve is, therefore, accompanied by a sudden rush of steam which may be of almost explosive violence.

55. **Laws of Ebullition.**—The general laws of boiling or ebullition may now be stated in the following form.

(i.) A liquid under a given constant pressure boils at a definite fixed temperature which remains constant for both liquid and vapour throughout the process. This temperature is the boiling point of the liquid under the given pressure.

(ii.) The boiling point of a liquid under a given pressure is the temperature at which the maximum pressure of its vapour is equal to the given pressure.

The normal boiling point of a liquid is its boiling point under the normal atmospheric pressure, and is a characteristic constant of the liquid.

56. **Latent Heat of Vaporisation.**—We have seen that when a substance changes from the liquid state to the vapour state it absorbs heat without rising in temperature, and when it changes from the vapour state to the liquid state it gives out heat without falling in temperature. These facts may be further illustrated by the following experiments.

Experiment 66.—Set up a water calorimeter ready for the measurement of heat. Boil some water in a flask fitted with a delivery tube and pass steam (at 100° C.) into the water in the calorimeter until the temperature rises to 100° C.

Here it is evident that the steam in condensing in the water in the calorimeter must give out sufficient heat in merely changing from steam at 100° C. to water at 100° C. (the final temperature of the condensed water) to raise the water in the calorimeter from its initial temperature to 100° C.

The experiment also indicates the possibility of measuring the heat given out by unit mass of steam in changing from steam at 100° C. to water at 100° C. For example, suppose the mass of water in the calorimeter to be 150 grammes, the water equivalent of the calorimeter to be 10 grammes, and the initial temperature of the water to be 10° C. Also suppose it is found from the increase in the weight of the calorimeter, that the mass of steam condensed is 28 grammes. Then the heat gained by the calorimeter is (160 × 90) units or 14,400 units; and if x denote the quantity of heat given out by one gramme of steam in condensing from steam at 100° C. to water at 100° C., the

heat lost by the 28 grammes of steam in condensing to water at 100° C. is 28 x units. We, therefore, get

$$28 x = 14,400,$$

or $$x = 514 \cdot 3 \text{ nearly.}$$

That is, this experiment gives the heat given out by one gramme of steam in changing from steam at 100° C. to water at 100° C. to be about 514 units.

It should be noticed that when steam at 100° C. condenses in water at a lower temperature the steam first *condenses* to water at 100° C., and this water then falls in temperature to the temperature of the mixture. Heat is, therefore, given out first by the steam in condensing to water at 100° C. and then by the condensed water in cooling from 100° C. to the temperature of the mixture. In the experiment considered above, the *final* temperature of the mixture is 100° C., so that *as a final result* the only heat given out in the calorimeter is the heat given out by the steam in condensing to water at 100° C.

Experiment 67.—Set up a water calorimeter as in the foregoing experiment. Let the water in it be at about 50° C.

Place a quantity of ether in a small flask with a long neck, or in a bulb with a fairly long stem.

Immerse the flask or bulb in the water in the calorimeter and let it remain there until the ether boils away, and is entirely converted into vapour.

It will be found that as the ether boils at a perfectly constant temperature (about 35° C.) it absorbs a large quantity of heat from the water in the calorimeter. That is, the ether in changing from the liquid state to the vapour state, absorbs heat without rising in temperature.

In this experiment where the temperature of the calorimeter is some degrees above its surroundings, the cooling effect should be determined and allowed for.

It will be seen that this experiment might be adapted to measure the quantity of heat absorbed by unit mass of the ether during vaporisation at its boiling point.

The heat which is thus absorbed during vaporisation of a liquid at constant temperature is known as the latent heat of vaporisation. It is transformed, as in the case of fusion, into molecular potential energy, and supplies the increase of molecular potential energy which attends the change from the liquid

state to the vapour state.   Some part of it, too, is expended in doing work against external pressure during the large increase in volume which accompanies the change in state.

The quantity of heat absorbed by unit mass of a liquid during vaporisation at its boiling point is called **the latent heat of vaporisation of the liquid,** or **the latent heat of the vapour.**

This definition is usually taken to apply to vaporisation at the normal boiling point under the normal atmospheric pressure. It may, however, be applied to vaporisation at any boiling point, or even to vaporisation at any *constant* temperature without actual boiling.   It will be found, however, that the value of the latent heat of vaporisation for any liquid varies with the temperature at which vaporisation takes place.   Experiment shows that in all cases the value decreases as the temperature rises.

The usual method of determining the latent heat of vaporisation of a liquid is an adaptation of the method of mixtures similar to that described below for the determination of the latent heat of vaporisation of water, or the latent heat of steam at 100° C.

Experiment 68.— Determine the latent heat of steam at 100° C. by the following method:—Fit up the apparatus shown in Fig. 66. A straight piece of thin-walled quill tubing, ABC, about 5 mm. diameter, is fitted through a short condenser tube, DE, in the manner shown in the figure.   The portion BC of the tube should be about 20 cms. in length, and a light screen, SS, of cardboard or wood should be fitted over the lower end of the condenser tube.

A small steam boiler provided with two supply tubes is set up at F, and one supply tube (the smaller of the two) is connected to the tube ABC at A, while the other supply tube is connected to the condenser tube at D.

In this way, when water is boiled in the boiler, the steam delivered through the tube ABC is passed through a steam jacket in the tube DE, and is, therefore, fairly dry and free from condensed particles when it issues from the tube at C.

An old oil can fitted with a cork carrying two delivery tubes will serve as a boiler, or two separate cans or flasks may be used.   There

is, however, a great advantage in using only one boiler for both supplies, in the fact that the supply through the tube ABC may be cut off or turned on at any time without affecting the pressure in the boiler. It is not desirable to make the same supply of steam serve both purposes; it is impossible to keep up an effective circulation in the jacket tube when this is done.

A screw clip, G, should be provided on the rubber tube bringing the steam from the boiler to the tube ABC.

When the apparatus is set up boil the water in the boiler vigorously, and let the steam pour through the tubes ABC and DE until they are all well heated.
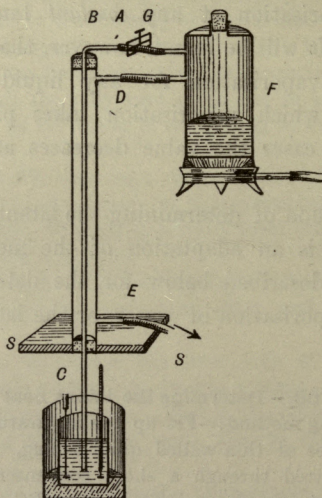
Fig. 66.

In the meantime, prepare a water calorimeter for the measurement of heat, and (for the same reason as in Exp. 48) make the last weighing of the calorimeter with sufficient accuracy to determine the weight to the nearest centigramme at least.

Now stop the current of steam through the tube ABC by means of the screw clip at G, place the calorimeter so that the end C of the tube dips well into the water, and then, after reading the temperature of the water in the calorimeter very carefully, turn on the supply of steam, and let it condense in the calorimeter till the thermometer shows a rise of 10° or 15°. When this rise of temperature is obtained

cut the steam *nearly* off ; remove the calorimeter, and note the final temperature of the mixture. Then weigh the calorimeter carefully, and find, from the observed increase in weight, the mass of steam which has been condensed.

From the data thus obtained the latent heat of steam at 100° C. may be calculated.

For example, let the data of an experiment be as follows :—

Mass of water in calorimeter, ...	160·2 grammes.
Water equivalent of calorimeter, . . .	9·8 ,,
Initial temperature of water, ...	10·2° C.
Final temperature of mixture, ...	22·4° C.
Mass of steam condensed, ...	3·41 grammes.

From these data we get the heat gained by calorimeter to be (170 × 12·2) units.

Also, the heat given out by the steam in condensing from steam at 100° C. to water at 100° C., and then by the water in cooling from 100° C. to 22·4° C. is

$$(3·41 \text{ L} + 3·41 × 77·6) \text{ units,}$$

where L denotes the latent heat of the steam.

We therefore have

$$3·41 \text{ L} + 3·41 × 77·6 = 170 × 12·2,$$
or $$3·41 \text{ L} = 1809·4,$$
or $$\text{L} = 530·6.$$

That is, this experiment gives the value of the latent heat of steam at 100° C. to be nearly 531 units. The correct value is about 537 units.

The cooling correction in this experiment can generally be avoided by arranging that the final temperatures of the mixture is as much above the temperature of the room as the initial temperature is below it.

It is difficult, however, to get a good result in making this determination. A serious source of error arises from the difficulty of drying the steam. The steam condensed in the calorimeter generally carries with it a considerable percentage of water at 100° C. in the form of a very fine spray, and the weight of this water is, by the method of the experiment, included in the weight of the condensed steam, although it gives up no latent heat. This error, in the mass of the condensed steam, may cause a very large error in the value of L for, as may be seen in the example given above, the total mass of the condensed steam is very small, and an error of only a gramme in its value may cause an error of nearly 50 per cent. in the final result.

It will now be understood that the tube ABC in the apparatus of Fig. 66 is jacketed with steam in order that the steam passed into the calorimeter may be as "dry" as possible.

Another form of this apparatus which is very easily set up is shown in Fig. 67. The inverted flask heated by a ring burner takes the place of the boiler, and the steam tube corresponding to ABC in Fig. 66 is jacketed by the vapour and water in the flask.

Regnault determined the latent heat of steam at 100° C. with great care, and found it to be about 537 units. He determined also the latent heat of steam at a number of other temperatures above and below 100° C., and found that the quantity of heat required to raise one gramme of water from 0° C. to any tem-
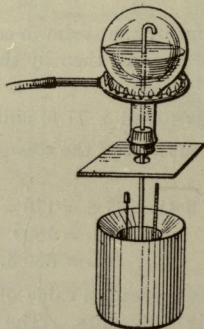
Fig. 67.

perature $t°$ C., and then to convert it into steam at that temperature, could be represented by the expression

$$H = 606\cdot5 + \cdot305\,t.$$

This quantity of heat was called by Regnault **the total heat of steam.**

It is plain that if L denote the latent heat of steam at any temperature $t°$ C., then

$$H = L + t,$$

and therefore $\qquad L = 606\cdot5 - \cdot695\,t.$

So that, when $t = 100$ we have

$$L = 606\cdot5 - 69\cdot5 = 537.$$

The latent heat of vaporisation of a number of liquids other than water may be determined by the method described above. The liquid is placed in the calorimeter, and the vapour from a quantity of the liquid kept boiling in a flask or small boiler is condensed in the calorimeter. The latent heat of vaporisation of the liquid can then be calculated from the data of an experiment in a manner exactly similar to that described above. In this case, however, it is necessary to know the specific heat of the liquid, for, if m denote the mass of condensed vapour, L its latent heat, T the boiling point of the liquid, M the mass of liquid in the calorimeter, t its temperature, w the water equivalent of the calorimeter, and θ the final temperature of the mixture, then

$$m\,\mathrm{L} + m\,s\,(\mathrm{T} - \theta) = \mathrm{M}\,s\,(\theta - t) + w\,(\theta - t),$$

where s denotes the specific heat of the liquid.

TABLE OF LATENT HEATS OF VAPORISATION.

Water, ...	536
Alcohol (ethyl), ...	205
Alcohol (methyl), ...	267
Sulphur, ...	362
Benzene, ...	93
Ether, ...	91
Turpentine, ...	74

A more satisfactory general method for any liquid is that due to Berthelot, who employed the apparatus shown in Fig. 68 for the determination of the latent heat of vaporisation of water and other liquids. A water calorimeter is used, and the vapour is condensed in a worm receiver immersed in the water in the calorimeter. This receiver, which can be detached from the rest of the apparatus, is weighed before and after an experiment, and the increase in weight at once gives the weight of vapour condensed. It will be seen that in this apparatus the vapour is condensed without coming into contact with

the water in the calorimeter, so that the method may be employed for almost any liquid.

It is desirable that the weight of the receiver should be comparatively small, in order that the weight of the condensed vapour may be determined as accurately as possible. The receiver is best made of thin copper or silver, but for certain liquids it would be necessary to use glass or platinum.
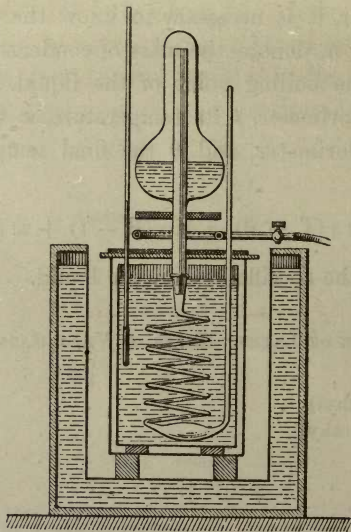
Fig. 68.—Berthelot's apparatus.

57. Change of Volume at Vaporisation.—When a substance changes from the liquid state to the vapour state at any temperature the change is, in general, accompanied by a very large change in volume.

Thus, in the case of water substance, the volume of one gramme of water at 100° C. is about 1·043 c.c., but the volume of one gramme of steam or saturated water vapour at the same temperature is about 1660 c.c. Hence, when water is converted into vapour at 100° C. there is an increase in volume of nearly 1660 c.c.

It must be noted, however, that as the pressure and temperature at which a liquid is vaporised are raised the density of the liquid decreases, and the density of the saturated vapour increases, until at a certain temperature the densities of the liquid and vapour become equal, and the two states become continuous.

This temperature is known as the *critical temperature* for the substance.

58. **Evaporation.**—The process by which a liquid gives off vapour at temperatures below its boiling point is called *evaporation*. As already explained, it is due to the escape of molecules at the surface of the liquid into the adjacent medium, and may, therefore, take place at all temperatures.

When evaporation takes place in a limited space it proceeds, as we have seen, until the space is saturated with vapour and the liquid and vapour are in equilibrium. When, however, evaporation takes place in an unlimited atmosphere, the process goes on continuously until all the liquid is converted into vapour.

> **Experiment 69.**—Dip a filter paper in water and expose it in the open air to "dry."
>
> It will be seen that all the water evaporates out of the paper in a comparatively short time, leaving the paper quite dry and free from water.
>
> **Experiment 70.**—Put a small quantity of alcohol in a watch-glass and expose it in the open air. The alcohol will quickly evaporate into the air.

The rate at which evaporation goes on into an unlimited atmosphere, such as the open air, depends upon a number of conditions. The pressure of the atmosphere is one of these conditions. The greater the pressure the less the rate of evaporation : we have seen, for example, that evaporation takes place almost instantaneously in a vacuum, but very slowly into air at the atmospheric pressure.

> **Experiment 71.**—Place a small quantity of water in a flask fitted with a cork and delivery tube. Connect the delivery tube to a filter

pump so as to reduce the pressure in the flask, and draw off the vapour as it is produced.

It will be found that the water evaporates completely in a very much shorter time than when exposed in the air at the ordinary pressure.

The rate of evaporation for any given liquid also depends upon the temperature. The higher the temperature of the liquid the greater is the maximum pressure of the vapour, and the greater, therefore, the rate at which molecules of the liquid escape from its surface.

Experiment 72.—Take two watch-glasses containing equal quantities of water and set one to evaporate in a warm place and the other in a cool place. It will be found that the water evaporates much more quickly in the warm place.

In comparing the rates of evaporation of different liquids at the same temperature it will be seen that, for the same reason, the rate for any liquid depends upon its boiling point. The lower the boiling point of a liquid the greater must be the maximum pressure of its vapour at a given temperature, and the greater, therefore, its rate of evaporation at that temperature.

Experiment 73.—Place equal quantities of water, alcohol, and ether in watch-glasses, and compare the time they take to evaporate completely under the same conditions.

It will be found that the ether evaporates in a few minutes, the alcohol takes a longer time, and the water a still longer time.

Another important factor which influences the rate of evaporation of a liquid into any atmosphere is the quantity of vapour already present in the atmosphere. If the atmosphere is quite free from vapour the evaporation goes on freely, but, if the atmosphere is saturated with vapour, then no evaporation at all takes place.

That is, the rate of evaporation of a liquid into any atmosphere depends upon the degree of saturation of the atmosphere with the vapour of the liquid.

This explains why the continuous renewal of the atmosphere in contact with the surface of a liquid promotes evaporation. The layer of atmosphere in contact with the liquid at any instant is removed before it becomes saturated and is replaced by a fresh layer. In this way evaporation goes on continuously into a comparatively "dry" atmosphere, and, therefore, goes on more rapidly than in a still atmosphere where the vapour passes by slow diffusion from the saturated layer in contact with the liquid to the less and less saturated layers surrounding it.

> **Experiment 74.**—Place equal quantities of water in watch-glasses. Set one to evaporate in still air, but direct a gentle current of *dry* air over the surface of the other.
>
> A current of dry air may be obtained by forcing a current of air with a foot bellows through a drying tube containing calcium chloride or pumice stone soaked in sulphuric acid. The current should issue from a wide tube so as to spread over the surface of the water.
>
> It will be found that evaporation goes on much more quickly under the influence of the air current.

For the same reason evaporation goes on more rapidly into a warm atmosphere than into a cold atmosphere. The higher the temperature of the atmosphere the greater is the quantity of vapour necessary to saturate it at that temperature, and the more rapidly it absorbs vapour when unsaturated or only partially saturated. A *warm* current of *dry*, vapour-free air would thus be specially helpful in promoting evaporation.

The rate of evaporation of a liquid under given conditions is found also to depend upon the extent of the surface exposed to the atmosphere. Experiment shows, however, that the rate of evaporation is proportional to the linear dimensions of the surface and not to its area.

> **Experiment 75.**—Place equal quantities of ether in shallow crystallising dishes of different diameters and set them to evaporate under the same conditions.
>
> It will be found that evaporation goes on more rapidly in the larger dish and that the rate of evaporation in the two cases is proportional, roughly, to the diameters of the dishes.

Experiment 76.—Place a small quantity of ether in a test-tube or small beaker and cause it to evaporate (a) by exposing it to the air, (b) by blowing a current of air through it.

It will be found that evaporation is much more rapid in the second case. The surface at which evaporation takes place is greatly increased, for evaporation takes place at the inner surface of all the bubbles formed. The bubbles thus become saturated as they pass through the liquid and carry off the vapour as quickly as it is formed.

The rate of evaporation must also depend in some measure on the rate at which the latent heat of vaporisation can be supplied during evaporation. When a liquid evaporates the latent heat is absorbed form the liquid itself and from its surroundings. If the containing vessel and its supports are good conductors of heat a considerable proportion of the latent heat may be absorbed from them, but if they are bad conductors, then practically all the heat comes out of the liquid itself, and the temperature of the liquid must, therefore, fall as evaporation proceeds.

The fall in temperature produced by the absorption of the latent heat of vaporisation from the liquid during evaporation is readily illustrated. If a few drops of ether or alcohol are poured on the palm of the hand, the cooling effect resulting from the rapid evaporation of the liquid and the consequent absorption of heat from the hand is very marked. This effect is shown in a more striking manner by the following experiment.

Experiment 77.—Put a quantity of ether in a small beaker of very thin glass and place the beaker on a sheet of cork so as to cover a drop or two of water which has been placed on the cork. Now blow a current of air through the ether so as to promote rapid evaporation. It will be found that in a few minutes the water between the bottom of the beaker and the cork freezes so that the beaker is firmly frozen to the cork.

It is possible even to freeze a liquid by the absorption of latent heat caused by its own evaporation. This was first demonstrated practically in the case of water by Leslie in an experiment now known as **Leslie's experiment.**

Experiment 78.—Put a small quantity of water in a wide shallow pan and place the pan under the receiver of an air pump resting on two strips of glass placed across the top of a larger pan containing strong sulphuric acid. Now exhaust the receiver. It will be found that as exhaustion proceeds the water rapidly evaporates and, it may be, boils under the reduced pressure. The water vapour is absorbed by the strong sulphuric acid as rapidly as it comes off so that the water quickly falls in temperature and ultimately freezes.

The same effect may also be exhibited by means of **Wollaston's cryophorus** as explained below.

Experiment 79.—Wollaston's Cryophorus, shown in Fig. 69, consists of a long closed tube with a bulb at each end, bent twice at right angles, as shown in the figure, and filled with water and water vapour only. The quantity of water in the tube should be sufficient to fill one of the bulbs about half full. The pressure inside the tube at any temperature is thus the maximum pressure of water vapour at that temperature.

Manipulate the tube so as to transfer all the water into one bulb, B, and then surround the bulb A with melting ice in a large beaker. The vapour in the bulb A is thus condensed, and is replaced as rapidly as it is condensed by evaporation from the water in the bulb B. That is, the water in B rapidly distils over into A, and the absorption of heat which accompanies the rapid evaporation of the water in B quickly lowers the temperature to freezing point and ultimately causes the water to freeze into a solid mass.
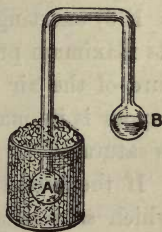
Fig. 69.

These experiments illustrate the principles applied in the construction of **freezing machines.** Carré's freezing machine, for example, is simply an elaboration of Leslie's experiment.

59. **Water Vapour in the Atmosphere.**—It is plain that large quantities of water vapour must always be present in the atmosphere. Evaporation is always going on from the surface of the large masses of water distributed over the surface of the earth, and the water vapour thus produced diffuses through the air and is carried by winds and air currents in all directions. The

distribution of vapour throughout the atmosphere may thus be somewhat irregular, and may vary in quantity at any given place from day to day, or even from hour to hour.

The quantity of water vapour present in the air at any given place is rarely sufficient to saturate the air. The air is generally unsaturated—that is, the vapour present is at less than its maximum density, and is exerting a pressure less than its maximum pressure at the existing temperature. The presence of vapour in the air can generally be demonstrated, however, by cooling the air until the temperature falls to a point at which the amount of vapour actually present in it is sufficient to saturate it. Thus, if the vapour present in air at 20° C. exerts a pressure of 9·1 mm. of mercury, it is evidently (see Table on p. 163) exerting a pressure which is only a little more than half its maximum pressure at this temperature; but if the temperature of the air is lowered to 10° C. then the pressure of the vapour is its maximum pressure at that temperature, and the air is saturated.

If the temperature of the air is lowered below the point at which saturation thus sets in, the vapour is at once condensed, either as *cloud* or *fog* in the air, or as *dew* on the surface of any cold body with which the air may be in contact.

The temperature at which the quantity of water vapour actually present in the air is sufficient to saturate it has therefore been called the **dew point**. The dew point of the air at any time may be determined conveniently and accurately by the method of the following experiment.

Experiment 80.—Obtain a cylindrical vessel of thin spun aluminium, about 10 cms. high and 6 cms. diameter, and having its outer surface well polished. Half fill this vessel with water a little above the temperature of the air, and provide it with a thermometer, reading to fifths or tenths of a degree, and a stirrer.

Then add a number of small pieces of ice to the water, and stir the mixture continuously as the ice melts.

As the temperature falls watch the outer surface of the aluminium

vessel carefully for the *first trace* of a deposit of dew on it. The temperature indicated by the thermometer when the deposit begins to form is the dew point. The observation should be repeated three or four times, and the mean of the results, after the first trial observation, taken as the dew point.

It is well to interpose a large sheet of glass between the observer and the aluminium vessel in making the observations.

It will be understood that in this experiment the air in contact with the outer surface of the aluminium vessel cools with the vessel, and when the dew point is reached, and the air saturated, the slightest lowering of temperature beyond this point causes the vapour to begin to condense on the surface of the vessel as a fine film of moisture. The presence of the film is readily detected by the dulling effect it has on the bright surface of the aluminium. It can also be detected by touching the surface with the tip of a feather.

The humidity of the atmosphere depends not so much on the actual amount of vapour present in the air as on the ratio of that amount to the amount which would saturate the air at its existing temperature. Thus, if the amount of vapour actually present in air at 20° C. is 8·6 grammes per cubic metre, its humidity is comparatively low, for it is only half saturated, the amount of vapour required to saturate air at this temperature being about 17·2 grammes per cubic metre. On the other hand, if air at 10° C. contains 8·6 grammes of vapour per cubic metre, then its humidity is very high, for the amount of vapour required to saturate air at 10° C. is about 9·4 grammes per cubic metre, and the air is therefore nine-tenths saturated.

This ratio of the amount of vapour actually present in the air to the amount required to saturate the air at the existing temperature is called the **relative humidity** of the air, and is used in specifying the hygrometric state of the air.

The relative humidity of the air can be determined by finding the dew point. Thus, if the dew point of air at 20° C. is found, by the method of Exp. 30, to be 10° C., then it is known that the vapour present in the air exerts a pressure equal to the maximum vapour pressure **at 10° C.** If the air were saturated, however, the vapour would exert a pressure equal to

the maximum vapour pressure **at 20° C.** Hence, assuming the quantity of vapour in the air to be proportional to the pressure it exerts, we have the relative humidity of the air given by the ratio $\frac{9\cdot1}{17\cdot4}$, for the maximum vapour pressures at 10° C. and 20° C. are 9·1 mm. and 17·4 mm. respectively. That is, the amount of vapour present is ·523 or 52·3 per cent. of the saturation amount.

It will be seen from this example that, in general, if F denote the maximum vapour pressure at the temperature of the air, and f the maximum pressure at the dew point, then the relative humidity is given by the ratio f/F.

As already indicated, the formation of *cloud*, *fog* or *mist*, and *dew*, is caused by the condensation of the water vapour in the air under different circumstances and conditions.

Cloud is formed by the cooling of large masses of air in the upper regions of the atmosphere below the dew point. The vapour condenses into very minute drops of water, or, it may be, into minute ice crystals, which cluster together and form the various cloud masses with which we are familiar. The cooling of the air may be caused by the meeting and mixture of warm and cold currents of air, but more commonly it is caused by the expansion of the mass of air as it ascends. The pressure decreases as the air ascends, and the work done by the air in expanding against external pressure causes an absorption of energy in the form of heat from the air, and so causes a lowering of temperature. An upward current of nearly saturated air may thus, at a certain height, be cooled below the dew point, and its moisture will then be condensed and become visible as a cloud. The huge piled-up masses of cumulus clouds are formed in this way, and the process of their formation may often be observed in progress. The minute drops of water which form some clouds are so small that they fall through the air very slowly. If, therefore, the drops which form a particular cloud persisted long enough, the cloud would settle slowly downwards

to the earth. It must be remembered, however, that a cloud is not a floating mass of unchanging material, the drops of which it is composed are continuously disappearing by evaporation and diffusion at its outer surface, and are continuously renewed by condensation from fresh supplies of moisture-laden air. A cloud which appears to occupy a fixed position may thus be only a continuously changing mass of condensed vapour formed in a fixed region in which the conditions which cause condensation prevail. The cloud formed at the mouth of the delivery tube from a flask in which water is boiling (Fig. 55) is an example of this. It is a constantly changing mass of condensed vapour which is continuously renewed by the supply from the flask, and continuously dissipated by evaporation and diffusion from its outer surface. Also, the position it occupies and the size to which it attains are determined by the conditions which lead to its formation, and by the fact that the loss from its outer surface must be equal to the gain from the jet of the flask. If the supply of vapour is stopped, the cloud at once decreases in size and quickly disappears. The cloud or mist which sometimes envelopes the top of a high mountain is an example of a cloud formed in this way. When warm air saturated with vapour comes near the cold mountain top it is cooled below the dew point, and the vapour condenses into a cloud or mist, which appears to be stationary, because it is renewed as quickly as it is dissipated.

When the atmospheric conditions are such that the droplets which compose a cloud increase in size and unite together to form larger drops, the clouds settle down towards the earth and assume the black appearance characteristic of *nimbus* or rain clouds.

If the drops in these clouds continue to grow in size the cloud may break up into small *raindrops*, which may increase in size as they fall and reach the ground as *rain*.

If the temperature is so low that the vapour freezes as it

condenses to form clouds, these clouds may break up into snow flakes and fall to the ground as *snow*.

The exact conditions which lead to the formation of *hail* are somewhat doubtful. Hailstones are generally made up of a number of concentric layers of ice and snow round a central particle of snow. They are probably formed when small snowflakes fall from a great height through layers of alternately warm and cold air.

Fog or mist is produced when large masses of still air are cooled below the dew point. The presence of minute particles of dust and smoke in the air greatly facilitates the formation of fog, for the particles form nuclei on which the vapour condenses in drops much more readily than in dust-free air. This explains the formation and the character of fogs in large towns. The drops of moisture which compose the fog are generally formed on particles of soot and dust as cores, and are, therefore, more or less opaque, and leave a dirty black deposit wherever they settle.

The fog banks formed near Newfoundland are caused by the condensation which results from the meeting of the warm current of saturated air which follows the gulf stream with the cold current which flows from the north along the Labrador coast.

The fog or mist which often forms after sunset over low-lying land and water is due to the cooling of the warm saturated air below its dew point. During the day the air is greatly heated and, if water is near it, may also be kept practically saturated with vapour; hence, when the sun sets and the air cools the temperature soon falls below the dew point and a fog is formed.

The formation of **dew** was first explained by Dr. Wells. Dew is deposited on the surface of the earth when the air in contact with the surface is cooled below its dew point. It is, therefore, generally deposited at night in still air after a warm day. During the day the surface of the earth is heated by the sun's rays, but after sunset it cools rapidly, and, if the air is stationary, the

layer in contact with the earth may be cooled below its dew point and the condensed vapour deposited as dew on the surface of the earth.

It will be seen that the conditions essential to the formation of dew requires a warm day followed by a clear, still night.

During the day the air becomes heated and can contain a considerable quantity of water vapour without becoming saturated. During the night, if the sky is clear, the surface of the earth cools very quickly by radiation into space, so that if the air is still the layer in contact with the earth cools with it and quickly reaches its dew point. If the night is not clear the earth does not cool so rapidly by radiation, and its temperature may not fall to the dew point, so that little or no dew is deposited on a cloudy night.

It is found that dew is not deposited to the same extent on all bodies on the earth's surface. It will evidently be deposited most copiously on bodies which have good radiating surfaces and are bad conductors of heat. These bodies will lose heat quickly by radiation, and cannot gain much heat from the earth or from surrounding bodies by conduction; they, therefore, cool very rapidly, and to a lower temperature than other bodies, and so receive a heavy deposit of dew on their surface. This explains why dew is deposited mainly on plants and grass: a plant or a blade of grass has a good radiating surface, and the material of which it is composed is of very low conductivity.

It has been shown by Aitken that the water vapour given off by the earth and the leaves of plants, in addition to the vapour actually present in the air, contributes in some measure to the formation of dew.

60. **Sublimation.**—It is found that certain solid substances change, when heated, from the solid state direct to the vapour state without passing through an intermediate liquid state. This process of direct change from the solid state to the vapour state is known as **sublimation**.

Experiment 81.—Heat a small piece of camphor in a test-tube and note the result.

It will be found that the camphor does not melt but vaporises (or *sublimes*), and condenses as a solid mass in the upper part of the test-tube.

Heat also a small quantity of **iodine** in a test-tube and note the result.

It will be seen that the solid iodine is converted into a beautiful violet vapour which condenses in the upper part of the tube as minute crystals.

The explanation of sublimation is comparatively simple. All solids probably give off vapour, and it is possible for a vapour to be in equilibrium with its solid in the same way as with its liquid. This explains why a solid substance can pass into vapour by evaporation. Snow, for example, disappears in windy weather by evaporation at temperatures below the freezing point. It is found, too, that clothes hung out to dry in the Arctic regions soon lose the coating of ice in which they are at first encased.

The maximum pressure of a vapour in equilibrium with its solid is, however, generally very low. Thus, the maximum pressure of water vapour in equilibrium with *ice* at 0° C. is 4 mm. In the case of some substances, however, the maximum pressure of the vapour when in equilibrium with the solid, is equal to one atmosphere at some temperature *below its melting point*. That is, when the substance is at its melting point the maximum pressure of its vapour is greater than one atmosphere, and the liquid, if it could be formed, would be at a temperature *above its normal boiling point*, and would, therefore, change to vapour as it formed.

A substance may, therefore, be said to sublime at any pressure, because its boiling point, at that pressure, is *below* its melting point. If, however, the pressure to which the substance is exposed is increased until the boiling point is above the melting point, the substance melts and vaporises in the usual way.

CHAPTER X.

CONDUCTION OF HEAT.

61. Conduction of Heat.—We have already noticed that when two bodies differing in temperature are placed in contact heat passes from the hot body to the cold body. Similarly, when two points in the same body differ in temperature heat is transferred through the substance of the body from one point to the other in the direction of the fall of temperature.

The process by which heat is transferred in this way from point to point through the substance of a body as a result of difference of temperature between the points is called *conduction of heat*, and the property of the substance which enables it to act as a conductor of heat is called *conductivity* or *thermal conductivity*.

Conduction of heat may take place in a solid, a liquid, or a gas, but it must be noted that the term applies only to the transfer of heat which takes place from particle to particle in a substance while the relative positions of the particles throughout the substance remain undisturbed.

In a solid, therefore, transfer of heat from point to point can take place only by conduction, but in a fluid heat may also be transferred from point to point by actual transfer of the heated portions of the fluid.

On the theory that heat is the molecular kinetic energy which a body possesses in virtue of the vibratory motion of its molecules, the process of conduction evidently consists in the communication of any increase in the energy of vibratory motion from molecule to molecule throughout the substance of the body.

Instances of the conduction of heat are familiar to all. The usual method of heating over a flame or over a fire is an example; the heat is conducted from the hot flame or fire to the colder substance to be heated through the thickness of the containing vessel. When one end of a poker is placed in the fire it is well known that while the end in the fire is getting red hot, heat is conducted along the poker outwards from this hot end towards the other colder end, and that a considerable length outside the fire is thus made too hot to touch. One frequently observes, too, that if boiling water is poured into any vessel the *outside* of the vessel quickly becomes too hot to touch. This shows that heat passes through the thickness of the vessel from the inner hot face to the outer and colder face.

It is also within the scope of ordinary observation that substances differ greatly in their conductivity for heat. The difference in the sensations experienced in touching different substances has already been referred to as an example of this. When we touch a substance at a temperature higher or lower than that of the hand the sensation of "heat" or "cold" is caused by heat being conducted from the substance to the hand in the one case, and from the hand to the substance in the other case. If the substance is of high conductivity the transfer of heat may, in either case, be considerable, and may cause, if the difference of temperature is sufficiently great, an intense and painful sensation. If, however, the substance is of low conductivity, the transfer of heat, even with a large difference of temperature, may be small, and the sensation experienced may be of very slight intensity. Thus, if a piece of hot or very cold metal is touched the sensation is painful, and may be attended with injury to the skin; but if a piece of wood or cloth *at the same temperature* is touched only a very slight sensation of heat and cold may be experienced. For the same reason since linen is a much better conductor of heat than cotton, linen sheets feel much cooler to the skin than cotton sheets, and linoleum, being a much

better conductor than carpet or matting or even than wood, feels colder to the feet than these substances.

It is possible with a little care to classify substances roughly in the order of their conductivity by means of the sensation experienced on touching then. If, for example, all the objects in a room are touched it is easy to decide that metals are good conductors, substances like paper, cloth, leather, poor conductors, and substances such as stone, marble, glass, china of moderate conducting power.

This difference in the conductivity of different substances may be further exemplified by the following experiments.

Experiment 82.—Get a wooden cylinder bound at each end with a heavy ring of copper or brass let in flush with the surface of the wood, wrap a piece of *thin* paper once round the cylinder, and let the flame of a Bunsen burner play over the paper.

It will be found that the paper quickly blackens and chars *over the wood*, but remains unchanged over the brass or copper rings. Copper being a very good conductor, conducts the heat away from the paper quickly enough to prevent scorching; wood, on the other hand, is a bad conductor, and the paper over it is quickly heated to the scorching point.

Try the same experiment with thick paper or with two or three layers of thin paper and note the result.

Experiment 83.—Get a cubical vessel with the sides and bottom made of sheets of copper, iron, lead, marble and glass of the same thickness fitted into a wooden frame. Fill the vessel with hot water, and after some time compare the sensation experienced in touching the outer surface of each side and the bottom.

It will be found that the substances may be arranged in order of conductivity as follows :—Copper, iron, lead, marble, glass, wood.

Experiment 84.—Obtain a heavy copper ring, similar to that shown in Fig. 70, and fit a number of similar rods of different materials into the holes drilled in its outer face as shown in the figure.

Before placing the rods in position they should be covered with a thin coating of paraffin wax by dipping them in hot melted wax, or a thin thread of sealing wax (easily obtained by drawing the wax out when hot) should be fixed lengthways on each rod by heating the rod till the thread adheres to it.

When a rod prepared in this way is heated at one end the conduction of heat along it will be indicated by the melting of the wax along the rod as the temperature at which wax melts is reached at successive points in its length. When the rods are in position heat the ring with a Bunsen flame in the manner shown in the figure.

As the heating proceeds it will be seen that at first the wax melts gradually along the rod, but that ultimately a stationary state is attained, and the point to which the melting has travelled along each rod becomes fixed.

On comparing the lengths to which the wax has melted along the different rods it will be found that they are very different, and as the length in each case depends upon the conductivity of the material of the rod, being greater the higher the conductivity, the different materials can be arranged in order of conductivity by placing them in the order indicated by these lengths.
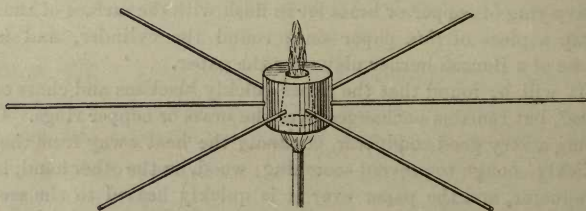
Fig. 70.

In this way it can, for example, be shown that of the metals in common use, such as iron, copper, lead, and brass, copper is much the best conductor of heat, and that the others follow at a considerable interval in the order brass, iron, lead.

The low conductivity of certain substances has many familiar applications. The handles of tools, such as a soldering iron, which are heated when in use, are made of bad conducting material, such as wood, to prevent them becoming too hot for the hand. Similarly the handles of flat-irons, kettles, tea-pots, coffee-pots, &c., are provided with "holders" of cloth or felt, or are made of some non-conducting material, such as wood, in order to protect the hand. In some cases where the handles of tea-pots or coffee-pots are made of metal they are separated from the rest of the vessel by discs of non-

conducting material, such as porcelain or china, in order that they may remain cool.

The effect of clothing of all kinds in keeping the body warm depends upon the low conducting power of the materials employed for the purpose. When the body is clothed or covered with material of low conductivity it loses the heat generated in it by physiological processes very slowly, and is thus easily maintained at its proper temperature. Flannel and silk, particularly the latter, are of very low conductivity, and are in other ways specially suited for underclothing. An eider-down quilt is practically a non-conductor of heat, and is also very light, so that it is specially useful as a bed cover.

The contrivance known as a *Norwegian cooking box* is another instance of the use of a substance of low conductivity for preventing loss of heat. It is a wooden box lined round the sides with a thick layer of felt and fitted with a lid also thickly lined with felt. The central space in the box is shaped to receive a metal vessel suitable for use in cooking, and when the box is closed the vessel is closely surrounded by a thick layer of felt. It is used for completing the cooking of partially cooked food, and for keeping the food hot until it is wanted. The food is prepared and partially cooked in the metal vessel which fits into the box, and, while the food is at the cooking temperature, the vessel is quickly transferred to the box and shut in. The loss of heat from the enclosed vessel is usually so small that the cooking is continued in the vessel for some time, and the food is kept hot for many hours.

A substance of low conductivity is as useful in preventing heat from entering a body as in preventing heat from leaving a body. Thus a "cosy" used in keeping a tea-pot hot, or a Norwegian cooking box, might equally well be used for keeping a piece of ice from melting. The covering prevents heat in the one case from passing out of the hot body, and in the other case from passing into the cold body. This explains why ice is

often wrapped in flannel or packed in sawdust to prevent it from melting.

An important application of high conductivity is found in the construction of the Davy safety lamp. It is found that the process of combustion in a flame cannot be maintained if the temperature of the flame falls below a certain point known as the ignition point for the gases in combustion. If, therefore, a good conductor of considerable mass is placed in contact with a flame it may conduct heat away from it with sufficient rapidity to lower the temperature below the ignition point, and so extinguish the flame. This effect of a good conductor on a flame is illustrated by the following experiments.

Experiment 85.—Take a narrow strip of copper and roll it, not too closely, into a tapering spiral.

Attach this spiral to a copper wire and suspend it over the flame of a candle or a bicycle lamp.

It will be found that if the spiral is lowered so as to surround the flame before it gets hot it puts the flame out, but if it is allowed to get hot before lowering it the flame is not extinguished.

This shows that the extinction of the flame is due to loss of heat by conduction into the cold spiral.

Experiment 86.—Take a piece of fairly stout copper wire gauze and lower it on to the flame of a Bunsen burner.

It will be seen that the flame does not extend above the gauze. The flame is not pressed down and made to spread laterally by the gauze, but appears to be extinguished from the top downwards as the gauze is lowered.

The gauze, being of good conducting material, conducts heat away from the flame so that the region in contact with the gauze is lowered in temperature below the ignition point. The flame is thus unable to extend upwards through the gauze, for the layer of gas in contact with the gauze is kept below the ignition point so long as the temperature of the gauze itself is not too high. If, however, the gauze is held in the flame until the portion in contact with the flame is heated to the ignition point, the flame at once extends to its initial dimensions and burns above and below the gauze.

Experiment 87.—Turn the gas on in a Bunsen burner, but do not light the gas. Hold a sheet of copper wire gauze over the mouth of the Bunsen tube and then light the gas *above* the gauze.

It will be seen that the flame appears above the gauze, but does not extend through it to the gas below until the temperature of the gauze rises to the ignition point.

The power of wire gauze of high conductivity to limit the extent of a flame was applied by Davy in the construction of his safety lamp for the use of miners. The lamp is constructed, as shown in Fig. 71, so that the flame is enclosed in a cylinder of wire gauze ; hence, if fire damp appears in a mine at a point where a lamp is in use the gas *inside the cylinder of gauze* is ignited, but the flame does not extend through the gauze to the explosive mixture of gas and air in the mine. At the same time the characteristic blue flame of the fire damp burning inside the gauze gives warning of the presence of fire damp in the mine, and steps are at once taken to avoid an explosion.

Fig. 71.

62. Conductivity of Liquids and Gases. —The conduction of heat in liquids is complicated by the convection currents which are set up when a liquid is heated from below. Thus, if water in a beaker is heated by a Bunsen flame in the usual way the heated water ascends and is replaced by colder water from adjacent layers. Ascending and descending currents, known as *convection currents*, are thus set up in the liquid, and the heat communicated by the flame is, by their aid, very quickly distributed throughout the mass of the liquid.

The distribution of heat in this way throughout the mass of a liquid by the aid of convection currents is generally known as *convection*. The process is, however, merely the transfer of heat by conduction, as in solids, aided by the distributing effect of the convection currents. The colder portions of the liquid are brought by the convection currents to the heating centre over the flame, and the heated liquid is then carried away by the
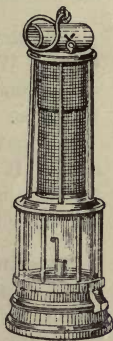
currents to mix with the colder portions and to be again brought back to the heating centre.

During this circulation of the liquid, however, the actual transfer of heat from the beaker to the liquid, and from any layer of the liquid to an adjoining colder layer, takes place by conduction.

If a liquid is heated from *above* it is evident that no convection currents can be set up in the liquid. The transfer of heat downwards through a liquid heated from above must, therefore, take place by conduction only. When liquids are tested for conductivity in this way it is found that, with the exception of mercury, all liquids are of very low conductivity.

Experiment 88.—Take a long test-tube and nearly fill it with water. Weight a small piece of ice by wrapping a short length of wire round it, and let it sink to the bottom of the water in the test-tube.

Now heat the water in the *upper* half of the test-tube over a small flame. It will be found that the water at the top of the column in the test-tube may be boiled for a long time without perceptibly heating the water below it or melting the ice at the bottom.

Experiment 89.—Get a cylindrical vessel of wood or guttapercha fitted, as shown in Fig. 72, with a thermometer at T, and a metal steam box at S.

The steam box forms a lid or cover to the vessel, and is removable, so that any given liquid may be placed in the vessel, and then heated from above by placing the steam box in position and passing a current of steam through it.

Test the conductivity of a number of liquids by placing them in this vessel, and noting the temperature indicated by the thermometer in each case after the steady state is reached.

It will be found that in all cases, the rises of temperature observed at T are very small, indicating that the liquids are of very low conductivity. If the rises of temperature are large enough to be compared, they give, by the order of their magnitude, the order of conductivity for the liquids.

The conduction of heat through gases is complicated by convection to an even greater degree than in liquids. It is

complicated also by radiation, for most gases allow radiation to take place through them. The transfer of heat between two surfaces, maintained at a constant temperature and separated by a layer of gas, may thus depend upon convection and radiation between the surfaces, as well as upon conduction. At low pressures, however, the convection effect practically disappears, and by separating the conduction and radiation effects at pressures below the convection limit, it is found that the conductivity of all gases is extremely low.

Experiment 90.—Let a drop of water fall on a red-hot metal plate, or into a platinum crucible or small evaporating basin heated to redness.
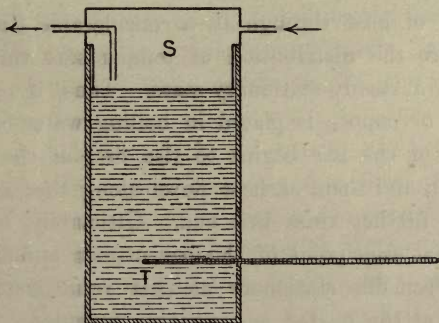
Fig. 72.

It will be found that the drop is not suddenly vaporised, as might be expected, but rolls about on the surface of the heated metal as a small spheroidal globule of liquid.

The temperature of the water is not raised even to the boiling point, for although it diminishes in quantity by gradual vaporisation it does not boil.

It can be seen on examination that the globule is not actually in contact with the hot metal, but is separated from it by a layer of its vapour, on which it rests as on a cushion.

The conductivity of this layer of vapour is, however, so low that the drop may persist in this *spheroidal state* at a temperature below 100° C. for a considerable time.

When the temperature of the metal plate falls to about 140° C., the rate at which heat reaches the water is not great enough to cause

vaporisation with sufficient rapidity to maintain a layer of vapour between the drop and the plate, for at this temperature the drop comes into actual contact with the plate, and is immediately vaporised.

The low conductivity of many substances, such as cotton wool, eider down, flannel, felt, &c., which are of loose open texture, and are permeated by air, although due in some measure to the want of continuity in their structure is mainly due to the low conductivity of the air which fills up the interstitial spaces in their structure.

63. **The Stationary State during Conduction.**— When a body is subjected to conditions of temperature which cause a flow of heat through it, a considerable time generally elapses before the distribution of temperature throughout the body attains a steady stationary state. Thus, if one end of a bar of iron or copper is placed in boiling water or steam, the temperature of the bar begins to rise, first at the end in the boiling water, and then, as heat flows along the bar, at points further and further from this end. Ultimately, however, the temperature at each point of the bar attains a final maximum value, and remains stationary at that value so long as the temperature at the heated end remains constant. The process by which this stationary state is attained at any point in the bar may be explained generally in the following manner. Imagine the rod divided into a number of thin transverse slices. During the *variable state* which precedes the *stationary state* any given slice receives heat by conduction from the adjacent slice on the hot-end side, and passes on heat by conduction to the adjacent slice of the cold-end side. The quantity of heat received by any slice in any given time is not, however, *all* passed on to the next slice. Some of it remains in the slice and causes a rise of temperature at that point in the bar, some of it is lost by cooling at the surface of the bar, and the remainder is passed on to the next slice.

This process goes on until the distribution of temperature along the bar is such that the difference of temperature between any two adjacent slices is sufficiently great to transfer all the heat which any slice receives to the next slice, diminished *only* by the loss by cooling at the surface of the slice. When this distribution of temperature is attained there can evidently be no further rise of temperature at any point in the bar, for all the heat that enters any slice is accounted for by the amounts passed on to the next slice and lost by cooling at the surface of the slice, and none, therefore, is available to produce rise of temperature in the slice itself.

It will now be understood from what has been said that the rate of rise of temperature at any point on the bar, or the rate at which any particular temperature "travels" along the bar during the variable state, depends on the specific heat and density of the material, as well as upon its conductivity. The greater the specific heat and the density of the material the greater will be the thermal capacity of a slice of the bar, and the more slowly will the temperature of the slice rise for a given supply of heat. Hence, if the material of the bar is of high thermal capacity per unit volume, the bar may, even when the material is of high conductivity, take a very long time to attain the stationary state, and the rise of temperature at any point in it may be very slow.

When the stationary state is attained, however, the final distribution of temperature along the bar depends only on the conductivity of the material, the dimensions of the bar, and the nature of its outer surface. The dimensions of the bar are involved, because the flow of heat along the bar will evidently depend upon its cross-section, and the loss of heat by cooling at the surface of the bar depends upon the extent as well as upon the nature of the surface.

In the stationary state the temperature must evidently decrease as the distance from the heated end (which is sup-

posed to be maintained at a *constant* temperature) increases. In a bar of given dimensions and surface, however, the decrease in temperature for any given increase in distance is smaller the greater the conductivity of the material, so that the temperature at any given distance from the heated end, or the distance from the heated end to which any particular temperature travels, is greater the greater the conductivity of the material. Thus, in Exp. 84 the distances to which the wax melts along the rods indicate the distances to which the temperature of melting travels along the rods, and when the stationary state is reached, the order of magnitude of these distances for the several rods indicates the order of their conductivities.

It will be clear, however, from what has been said, that in an experiment of this type the rods must be exactly equal in dimensions, and exactly similar in the character of their surfaces, and that any data derived from the distribution of temperature along the bar must be taken after the stationary state is attained. During the variable state the changes of temperature which take place in a rod involve, as explained above, the specific heat and density of the material as well as its conductivity, and give, therefore, no reliable indication of the conducting power of the material.

Experiment 91.—Repeat Exp. 84 with exactly similar rods of iron, bismuth, and aluminium, and notice carefully (*a*) how the melting of the wax proceeds during the variable state, and (*b*) the distance to which the melting extends when the stationary state is attained.

Look up the densities, specific heats, and conductivities of these three metals, and note if the observations made are consistent with the theoretical explanations given above.

Experiment 92.—Repeat the foregoing experiment with several rods of the same material and of exactly similar surface, but of different diameters.

Four or five pieces of brass wire (Nos. 6-10 S.W.G.) will serve the purpose well. The surfaces of the rods should be made alike by polishing them.

It will be found when the stationary state is attained that the wax is melted to a different distance along each rod, the distance being greatest on the rod of greatest diameter.

This shows that in comparing conductivities by this method the rods should be of the same dimensions.

Experiment 93.—Repeat the experiment again with several rods of the same material and dimensions, but differing in the nature of their surface. Three lengths of No. 6 brass wire may be taken, and the surface of one may be brightly polished, that of the second "black-leaded," and that of the third coated with soot from a smoky flame.

It will be found that when the stationary state is attained the wax is melted to different distances on the three rods. The polished surface allows comparatively little loss by cooling, the black-leaded surface allows a good deal more loss, and the sooted surface allows more loss still. It follows, therefore, from what has been said, that the wax will have melted furthest on the polished rod and least on the sooted rod.

This experiment shows that, in comparing conductivities by this method, the surfaces of the rods should be exactly similar in character.

64. Absolute Thermal Conductivity.

—It is assumed in the theory of conductivity that the flow of heat in any substance between two points very close together and differing in temperature by a very small amount is directly proportional to the difference of temperature and inversely proportional to the distance between the points.

It follows from this that if a very thin plane layer of any substance of uniform thickness, x, has its faces maintained at constant temperatures, differing by a small constant value θ, the flow of heat through the layer from one face to the other is proportional to the ratio $\dfrac{\theta}{x}$. The flow of heat through the layer is also, on first principles, directly proportional to the time in which the flow takes place, and also to the area across which it takes place. The flow of heat through the layer in a time t over an area A is, therefore, directly

proportional to A, t, and $\dfrac{\theta}{x}$, and, if H denote this flow of heat, we have:

$$H = k \left(A \cdot t \cdot \frac{\theta}{x} \right).$$

where k is a constant which depends in value upon the substance of the layer. This constant, k, is called the **absolute thermal conductivity** of the substance.

The ratio $\dfrac{\theta}{x}$ in the relation given above is called the gradient of temperature for the layer. It is evidently the difference of temperature per unit thickness of the layer, and is obtained by dividing θ, the difference of temperature between the faces of the layer by x, the thickness of the layer, **when both θ and x are very small.** The relation,

$$H = k \left(A \cdot t \cdot \frac{\theta}{x} \right)$$

as given above, applies, therefore, only to a *very thin layer* for which both θ and x are necessarily very small. It may, however, be taken to apply to a thick plate or wall of the substance if the conditions are such that the heat flows through the plate at right angles to its faces. That is, if all the heat which enters the area A on one face passes normally through the plate, *without suffering any loss in a lateral direction*, and emerges from the corresponding area A on the other face. If we suppose a plate through which heat flows in this way at right angles to its faces, to be divided in a large number of thin parallel layers, it is evident that the flow of heat through every layer is the same, and that the gradient of temperature is, therefore, the same for every layer. That is, the gradient of temperature along the thickness of the plate is *uniform*, and may, therefore, be found by dividing the difference of temperature between the faces of the plate by the thickness of the plate.

If, therefore, a plate or wall of any substance of thickness d has its faces maintained at constant temperatures, t_1 and t_2 respectively, the normal flow of heat in time t across any face area A, is given by

$$H = k\,A\,t\left(\frac{t_1 - t_2}{d}\right),$$

where k denotes the absolute conductivity of the material.

If, in this relation, we put A = 1, $t = 1$, $t_1 - t_2 = 1$ and $d = 1$, we have

$$H = k.$$

The absolute thermal conductivity of any substance may, therefore, be defined as *the flow of heat in unit time, across unit area of a plate of the substance of unit thickness, when there is one degree difference of temperature between the faces of the plate, and the conditions are such that the flow of heat is normal to the faces of the plate.*

It is difficult to realise in practice the conditions of normal flow through a plate. The flow through a small area at the centre of a large plate having its faces maintained at constant temperatures is, however, practically normal to the faces of the plate. If the edge of the plate is sufficiently distant at all points from the boundary of the area considered the lateral loss at the edge has no appreciable effect on the direction of flow across the central area.

The flow of heat across a plate which has its edge covered with a layer of some material of very low conductivity is also practically normal. The covering prevents loss of heat at the edge, so that practically all the heat which enters the plate through one face emerges through the opposite face.

The quantities involved in the relation

$$H = k\,A\,t\left(\frac{t_1 - t_2}{d}\right)$$

are usually expressed in C.G.S. units. That is, H is expressed in calories, A in square centimetres, t in seconds, d in centimetres, and the temperatures t_1 and t_2 in the Centigrade scale.

The experimental methods of determining the absolute thermal conductivity of a substance cannot be dealt with here.

The following experiment, however, indicates a simple and fairly accurate method of determining the absolute conductivity
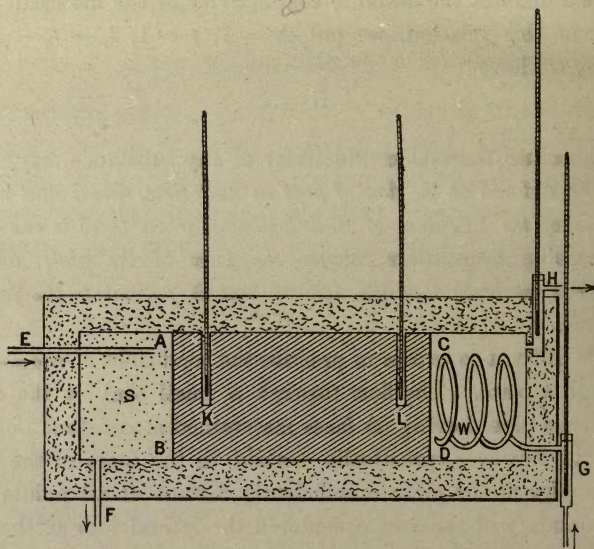
Fig. 73.

of a metal or other good conducting solid, and illustrates the theoretical matters dealt with above.

Experiment 94.—Determine the absolute conductivity of copper by means of the apparatus shown in Fig. 73. In the figure, ABCD represents a short cylindrical bar of copper about 5 cms. in diameter and 10 cms. in length. It is fitted with a brass steam box, S, at one end and a water box, W, at the other end. The steam box is provided with an inlet and outlet pipe at E and F respectively, so that a rapid current of steam can be maintained through the box. The water box is provided with inlet and outlet chambers at G and H respectively,

so that a slow current of water can be maintained through the box and the temperature of the water taken on entering the box by a thermometer in the inlet chamber, and on leaving the box by the thermometer in the outlet chamber. In this case the pipe from the chamber G does not open directly into the water box but is continued into a long spiral worm inside the box, as indicated in the figure. The outer surface of this apparatus is completely covered with a thick layer of felt which prevents cooling at the surface of the bar and minimises loss of heat from the steam and water boxes.

At two points K and L in the bar, near the faces AB and CD respectively, two radial holes are drilled to a depth a little greater than the radius of the bar for the reception of two thermometers which should read accurately to fifths of a degree. The holes should be as small as possible and a little mercury should be placed in them to make good contact between the thermometer and the bar.

In order to make a determination of the conductivity of the bar with this apparatus, a rapid current of steam is passed through the steam box and a slow current of water is maintained through the water box until the stationary state of conduction through the bar is attained.

When the steady readings of the thermometers at K and L and at G and H indicate that this state is attained, the readings of each of the four thermometers should be noted and the mass of water which leaves the water box per second should be carefully measured. Let t_1, t_2, t_3, t_4 be the observed temperatures at K, L, G and H respectively, and let m be the mass of water which passes through the water box per second. If, in addition to these data, the diameter of the bar and the distance between the axes of the holes at K and L are known the absolute conductivity of the material of the bar can be calculated. For, in the relation,

$$H = k \, A \, t \left(\frac{t_1 - t_2}{d} \right),$$

if we take t to be 1 second, we have :

$H = m \, (t_4 - t_3)$ for the heat received in the water box is sufficient to raise m grammes of water per second from t_4° C. to t_3° C.,

$A = \pi r^2$, where r is the radius of the bar,

$(t_1 - t_2)$ is the difference of the temperatures observed at K and L, and

d is distance between the axes of the holes at K and L.

The value of k is, therefore, given by the relation,

$$k = \frac{H d}{A \, t \, (t_1 - t_2)},$$

in which all the quantities involved are known.

It is important to notice here that the gradient of temperature in the bar $\left(\dfrac{t_1 - t_2}{d}\right)$ cannot be determined by taking t_1 as the temperature of the steam in the steam box, and t_2 the temperature of the water in the water box, and d as the length of the bar between the faces AB and CD.

Experience shows that when the bar is of good conducting material the faces of the bar or plate are not at the same temperature as the liquid or vapour with which they are in contact, and that the difference in temperature between the faces is much less than the difference between the fluids in contact with them. This explains why it is necessary in this experiment to introduce the thermometers at K and L.

Numerical Example.—In an experiment of this kind for the determination of the absolute conductivity of copper the following data were obtained.

The temperatures observed when the steady state was attained were :—

$$t_1 = 72 \cdot 6° \text{ C.,} \qquad t_2 = 36 \cdot 2° \text{ C.,}$$
$$t_3 = 10 \cdot 2° \text{ C.,} \qquad t_4 = 15 \cdot 6° \text{ C.,}$$
$$m = 20 \text{ grammes (per second),}$$
$$A = 20 \text{ sq. cms.}$$
and $$a = 6 \text{ cms.}$$

From these data we get :
$$H = 20 \ (15 \cdot 6 - 10 \cdot 2)$$
$$= 20 \times 5 \cdot 4$$
$$= 108 \text{ (in calories),}$$
and $$(t_1 - t_2) = (72 \cdot 6 - 36 \cdot 2) = 36 \cdot 4.$$

So that,
$$k = \frac{H \, d}{A \, t \, (t_1 - t_2)} = \frac{108 \times 6}{20 \times 1 \times 36 \cdot 4}$$
or $$k = \cdot 89.$$

That is, the absolute conductivity of copper is found by this experiment to be $\cdot 89$ in C.G.S. units.

The foregoing experiment illustrates the general principles involved in the measurement of absolute conductivity. The method of the experiment, however, is suitable only for a metal of high conductivity, and must not be considered as typical of the methods that have been employed for the experimental

determination of absolute conductivity. Different methods have to be adopted for solids which differ greatly in conductivity, and special methods have to be devised for the determination of conductivity in liquids and gases.

The absolute thermal conductivity of a great many substances have been determined experimentally by various methods, but the results obtained are found to differ considerably for different specimens of the same substance. Small differences in composition or in physical condition, and, in elementary substances, small traces of impurities appear to have a very considerable effect on the conductivity of a substance. It is found, too, that for any given substance the conductivity varies slightly with the temperature. Thus, iron at 100° C. conducts heat a little better than at 0° C.

The following table gives approximate representative values for some of the common substances.

Table of Absolute Thermal Conductivities in C.G.S. Units.

Solids.

		Marble,	·0071
Silver, .	1·0 – 1·2	Marble,	·0071
Copper,	0·7 – 1·1	Slate, .	·0048
Gold, .	0·7	Glass, .	·0024
Zinc, .	·3	Sulphur,	·0007
Tin, .	·25	Shellac,	·0006
Platinum,	0·2	Paraffin wax,	·0006
Iron, .	0·16 – 0·2	Mahogany, .	·00047
Nickel,	·13	Ebonite,	·0004
Lead, .	·08	Paper,	·00031
Bismuth,	· ·02	Cork, .	·00013
Brass, .	·26	Linen, .	·00021
German silver,	·11	Flannel,	·00015
Steel (hard),	·06	Cotton,	·00014
,, (soft), .	·11	Silk, .	·00012
		Baize, .	·00012
		Wool, .	·00012
		Cotton wool,	·00011
		Eider down,	·00011

Liquids.

Mercury,	. . .	·0200	Ethyl alcohol,	. .	·0004
Water, .	. . .	·0014	Aniline,	. . .	·0004
Glycerine,	. . .	·0007	Ether, .	. . .	·0003
Methyl alcohol,	. .	·0005			

Gases.

Air,	. . . .	·00005	Hydrogen, . . .	·00034

65. **Determination of Relative Conductivity.**—The experimental determination of the absolute conductivity of a solid is a somewhat difficult matter, but the determination of the
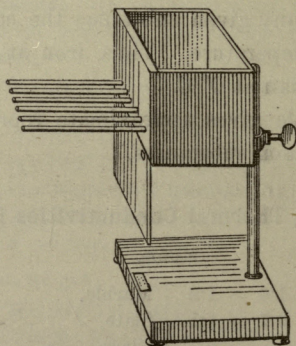
Fig. 74.

relative conductivities of a number of given solids may be made easily and with fair accuracy by means of a simple apparatus due to Ingenhousz.

This apparatus is shown in Fig. 74. It consists of a metal trough fitted with a row of holes in one face, through which rods of the materials to be compared are fixed as shown in the figure. The face through which the rods are fitted should be of fairly thick copper or brass, and the rods should taper slightly at one end so as to fit directly into the holes without the use of corks. The trough is filled with water or oil, to be maintained at a constant temperature, and the rods are fitted through the

side of the trough so that their ends inside the trough are in contact with the liquid.

For the reasons explained in Art. 63 the rods must all be of exactly the same diameter,* and their surfaces must be exactly similar in character. In the case of metal rods it is best to silverplate or nickelplate the surfaces; for other substances it is probably simplest to blacklead them.

A fine thread of sealing wax is fixed lengthways along each rod, as explained in Exp. 84, or a narrow longitudinal groove cut in each rod is filled with paraffin wax.

When the liquid in the trough is heated to constant temperature the ends of the rods are maintained at this temperature, and heat is conducted outwards from the trough along each rod. When the steady state is attained, the wax will have melted to different distances along the different rods, and by measuring these distances carefully the relative conductivities of the rods can be determined.

It can be shown that for similar rods maintained at the same constant temperature at one end, under exactly similar conditions, the relative conductivities of the rods are directly proportional to the *squares* of the distances to which any particular temperature travels along the rods. In this case, therefore, the conductivities of the rods will be directly proportional to the squares of the distances to which the temperature of melting wax travels along the rod. The distances should be measured from the front of the metal face into which the rods are fitted.

Numerical Example.—In an experiment with Ingenhousz's apparatus, the conductivities of iron, brass, and copper were compared. It was found that the distances to which the wax was melted on the rods were 7·1 cms. on the iron rod, 8·6 cms. on the brass rod, and 17·1 cms. on the copper rod. From these distances we

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* The rods need not be of the same *length ;* it is desirable, in fact, for the length to increase with the conductivity.

find that the conductivities of iron, brass, and copper are proportional respectively to

$$(7{\cdot}1)^2,\ (8{\cdot}6)^2,\ \text{and}\ (17{\cdot}1)^2.$$

That is, the relative conductivities of iron, brass, and copper are approximately in the ratio $1 : 1{\cdot}48 : 5{\cdot}95$, or roughly in the ratio of $2 : 3 : 12$.

It will be seen that this method cannot be used directly for substances which differ widely in conductivity. If a number of substances are to be compared by this method they must be divided into groups so that the range of conductivity in any one group is not beyond the range of the method.

The relative conductivities of liquids can be determined in a similar way by the method of Exp. 89, with the apparatus indicated in Fig. 72. If the thermometer is fitted through the bottom of the vessel the position of the bulb can be adjusted to read the same temperature for different liquids in the steady state, and the distance of the bulb from the surface of the liquid can then be measured for each liquid.

CHAPTER XI.

CONVECTION.

66. Convection Currents.—Convection currents are set up in any mass of fluid when the hydrostatic equilibrium in the fluid is disturbed by unequal heating or cooling. When any portion of the fluid becomes denser than the surrounding fluid it is acted on by forces which urge it vertically downwards, and, similarly, when any portion becomes less dense than the surrounding fluid it is acted on by forces which urge it vertically upwards.

Hence when a quantity of liquid in a large vessel is heated from below convection currents are at once established in the liquid ; the heated portions expand, and, becoming less dense than the surrounding liquid, rise in a vertical current from the centre at which heat is supplied to the liquid. At the same time the liquid thus displaced from below is replaced by colder liquid from the surrounding mass, and downward indraught currents are established towards the heating centre.

Similarly, if the surface of a mass of liquid is cooled, the cooled layers sink and are replaced by warmer liquid from below. A system of convection currents similar to that set up by heating the liquid from below is thus established.

In the same way if a gas flame is lit in a room the air in immediate contact with the flame is heated and ascends. At the same time this air is replaced by an indraught of air towards the flame from other parts of the room, and a system of convective circulation is quickly established in the room.

When a fire burns in the open air on a still day the upward current of heated air from the fire can easily be detected by the hazy and irregular outline of objects seen through it.

Experiment 95.—Take a large wide beaker and fill it nearly with water. Then pulp some good filter paper in a mortar and mix the pulp with the water in the beaker.

Heat the beaker with a small Bunsen flame from below, and note the convection currents set up in the water by following the motion of the paper pulp.

It will be found, as indicated in Fig. 75, that a vertical upward current ascends from the point where the flame is applied, and that downward indraught currents set towards this point from the surrounding body of water.

Fig. 75.

Experiment 96.—Fill the beaker with water and pulp as in the foregoing experiment. Then half fill a small beaker or test-tube with a freezing mixture, and let it float, centrally, on the surface of the water in the beaker.

It will be found that a system of convection currents, exactly the reverse of that in the foregoing experiment, is established. The central current is vertically downwards, and the external indraught currents are upwards.

Experiment 97.—Hold a piece of smoking paper near and over a Bunsen flame, and note the strong upward current of air which ascends from the flame.

Local convection currents are often produced in the open air on a hot day. When a stretch of rock or sand or shingle is very strongly heated by the sun's rays it heats the air in contact with it and sets up convection currents in the overlying air. The existence of these currents explains the hazy and tremulous appearance of objects seen through the air over the heated surface.

Convection currents are set up also in lakes and ponds of still water during cold weather. The surface layer of the water is cooled, and sinks, to be replaced by water from deeper layers.

When the temperature of the water reaches 4° C., the temperature of maximum density, convection ceases, as explained in Art. 28, and the surface layer cools progressively until it freezes, if the temperature falls low enough.

67. Distribution of Heat in a Fluid by Convection.— It has already been explained that heat is distributed very rapidly throughout any mass of fluid by convection.

When heat is supplied to a mass of fluid at any point, the whole mass is heated uniformly as it circulates past the point of supply, and the temperature of the fluid rises gradually and uniformly throughout its mass. Similarly, when a mass of fluid loses heat at any point the temperature falls gradually and uniformly throughout the mass. This distributing effect of convection in fluids more than compensates for their low conductivity, and heat may be transferred from point to point more rapidly by convection in a fluid of low conductivity than by conduction in a solid of high conductivity. Water may, for example, be boiled over a Bunsen flame in a thin paper vessel without damage to the paper. The heat supplied is carried away from the paper by the water with sufficient rapidity to prevent scorching.

The rapidity with which a mass of fluid gains or loses heat by convection, and the effect of convective circulation in maintaining uniformity of temperature throughout the mass during rise or fall of temperature makes a fluid substance specially suitable for use in thermometers. Mercury has special advantages in these respects. It is a liquid, and of high conductivity for a liquid; it therefore gains and loses heat rapidly, and uniformity of temperature is effectively maintained throughout any given mass of it. These effects of convection are, however, specially marked in gases, and for this reason among others already mentioned, a gas such as air, hydrogen, or nitrogen, forms the ideal thermometric substance.

When a hot body cools in air or in any gas, the cooling is

due partly to radiation, but mainly to convection. The hot body acts as a source of heat in the gas, and the convection currents set up round it carry away heat from the body very rapidly and distribute it throughout the surrounding gas. The magnitude of the cooling effect due to convection evidently depends to some extent on the specific heat of the gas, for the heat carried away from the hot body by a given mass of gas depends upon the specific heat of the gas. In confirmation of this it is found that a hot body cools more rapidly in hydrogen than in any other gas.

68. **Winds.**—It appears to be made out with some certainty that winds are convection currents on a large scale in the atmosphere. The currents are, in some measure, the result of the unequal heating of the earth's surface by the sun's rays. They are due also very largely to the unequal distribution of water vapour in the air. Air containing a large proportion of water vapour is less dense than drier air at the same temperature, so that a mass of air saturated with water vapour may be specifically lighter than the surrounding air. Rapid and plentiful evaporation at any point on the earth's surface may thus produce an upward convection current at that point. Currents of this kind, when they reach a great height, frequently give rise to huge masses of cumulus clouds by the condensation of the vapour which they contain.

It will be seen, however, that these two causes of convection currents in the atmosphere are supplementary to each other, and not antagonistic. The region of the earth's surface which is most intensely heated is also, where water is available, the region of most rapid evaporation.

The earth's surface in the region of the equator is much more intensely and uniformly heated than the surface in the temperate and arctic zones. The air in contact with the earth's surface near the equator therefore becomes intensely heated, and, when water is present, it also becomes heavily charged with water

vapour. This air is, therefore, displaced upwards by cooler air which flows in towards the equator from the north and south.

A general upward convection current is thus established in the air over the equatorial region, and the heated and saturated air carried away by this current is replaced by indraught currents which flow over the surface of the earth from the north and south towards the equator.

A general system of convective circulation is thus set up in the atmosphere.

The current which ascends from the equatorial region divides at a great height into two main currents, which flow north and south respectively as high-level currents, and so replace the air which flows in over the surface of the earth toward the equator.

This flow of air at a low level from the north and south towards the equator gives rise to the winds known as **the trade winds**. These winds should apparently be directly from the north in the northern hemisphere, and directly from the south in the southern hemisphere. The rotation of the earth from west to east has, however, an important effect on their direction relative to the earth's surface. The speed of a point on the earth's surface from west to east depends upon the position of the point, and evidently increases as the point approaches the equator. A current of air flowing *towards* the equator moves, therefore, over points whose speed of rotation from west to east gradually increases, and as the air in the current retains the speed it had at the point from which it started, it gradually lags behind the points over which it passes, and thus acquires an easterly component relative to points on the earth's surface.

The direction of the trade winds in the northern hemisphere is therefore from the *North-East*, and in the southern hemisphere from the *South-East*.

These winds prevail between the latitudes 3° N. and 35° N. in the northern hemisphere, and between 3° S. and 30° S. in the southern hemisphere. These limits vary within narrow limits

with the seasons, but rarely extend beyond 35° N. and 30° S. During the northern summer the northern and southern trade winds move a few degrees northwards, and at one point the southern winds cross the equator into the Pacific east of China, and give rise to a south-west wind known as a *monsoon*. Similarly, in the southern summer the trade winds move a few degrees southwards, and at a point in the Indian Ocean the northern winds cross the equator and give rise to the North-west monsoon in the Indian Ocean.
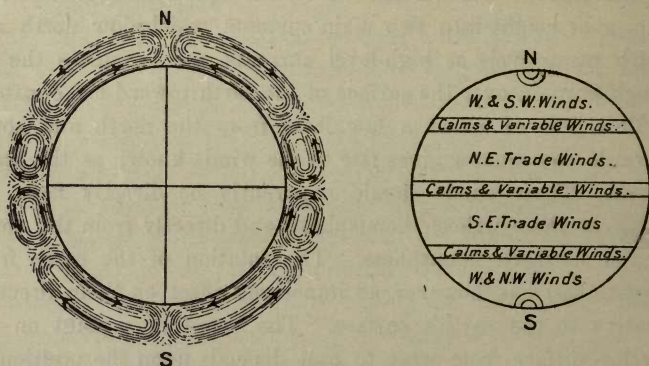
Fig. 76.

The upper high-level currents north and south from the equator, sometimes called the *upper trades,* come to the surface of the earth about latitude 35° N. and 30° S. In passing *from the equator* towards the poles these currents evidently acquire a westerly component relative to points on the earth's surface.

The upper trade is thus a south-west current in the northern hemisphere and a north-west current in the southern hemisphere.

The general system of atmospheric circulation, of which the trade system just described is the main element, is indicated diagrammatically in Fig. 76. The irregular distribution of land and water over the surface of the earth causes many disturbances

and irregularities in this system, but it may be taken as a general representation of observed facts.

Land and Sea Breezes are examples of local winds produced on a comparatively small scale by convection. They occur at places on the coast where the daily range of temperature is somewhat great. During the day the land is heated to a much higher temperature than the sea. The air over the land is, therefore, displaced upwards by an indraught of cooler air from over the sea. This indraught current is felt during the day as a *sea breeze*. During the night the land cools to a lower temperature than the sea, and ultimately the warmer air over the sea is displaced upwards by a colder air from the land. This current of cold air from the land to the sea is known as a *land breeze*.

These breezes can be observed only when the air is still and not disturbed by wind associated with the general circulation of the atmosphere.

69. Ocean Currents.—The surface currents of the ocean are caused by the action of the prevailing winds on the surface of the water. The main currents thus produced are split up and divested into many diverging branches by the action of the land masses on which they impinge, but the general system of surface currents can be traced directly to the action of the winds. The trade winds which blow steadily to the south and west in the northern hemisphere, and to the north and west in the southern hemisphere, combine to produce the great *equatorial current* which is found flowing round the earth westwards in the Atlantic and Pacific Oceans. In the Atlantic this current is split by the north-east point of the South American Continent, and the main northerly branch after flowing round the Gulf of Mexico flows in a north-easterly direction through the North Atlantic as the Gulf Stream.

In addition to these surface currents there is, however, a general circulation of the waters of the great communicating oceans which is due to convection.

This circulation is known as *vertical oceanic circulation*; it was first suggested by Lenz and was confirmed later by observations of deep sea temperatures.

It is found that the temperature at any depth greater than about 500 fathoms is practically the same everywhere in the communicating oceans. At this depth the temperature is only a few degrees above freezing point, about 40° F., and is found to fall slightly as the depth increases.

The surface waters, however, to a depth varying from 100 to 500 fathoms differ greatly in temperature, and are much warmer in the equatorial region than in the Polar Seas.

It follows from this that at any given depth, say 600 fathoms, the pressure in the Polar Seas is greater than in the equatorial waters, and a gradual flow of water below this depth is thereby produced from the poles towards the equator.

The water that is thus displaced from the Polar Seas is replaced by a general surface drift of water from the equator towards the poles.

This circulation may be illustrated by the following experiment.

> **Experiment 98.**—Open a door between a warm room and a colder room or passage, and test, with a candle flame, the direction of the air current at the top and bottom of the doorway.
>
> It will be found that the current at the bottom flows from the cold room to the warm room, and at the top from the warm room to the cold room.

The deep currents of cold water from the poles towards the equator acquire a westerly component as it flows southwards and ultimately flows to the south-west. Similarly, the surface flow northwards acquires an easterly component and gradually takes a north-easterly direction.

The water which flows as a deep current from north and south towards the equator rises towards the surface at the equator. The flow is a very gradual one, and the water is

:d as it rises, but notwithstanding this, water at 40° F. is . to be at a depth of only 300 fathoms at the equator. found, too, that the deep-lying cold water comes very near surface along the eastern coasts of the great continents. deep currents of the ocean being towards the *south-west*, rge up to the surface along the *east* coast of any mass of nd which they meet.

70. **Ventilation.**—A system of ventilation aims at establishing a steady and continuous circulation between the outer air and the air in the building to be ventilated. The circulation should be effected without causing draughts, and the air admitted to the building should, when necessary, be warmed and purified.

An essential condition necessary for the maintenance of any system of circulation of air in a room or building is the provision of suitable and adequate means of inlet and outlet for the flow of air through the building. This point is illustrated by the following experiment.
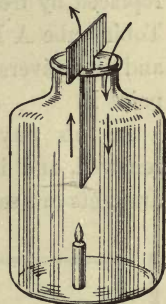
Fig. 77.

Experiment 99.—Take a large flask or jar and set a short length of candle on the bottom of it. Light the candle and notice what happens. It will be found that although the air in the flask is in free communication with the outer air, the candle soon goes out for want of air.

Now place a strip of cardboard vertically in the neck of the flask as shown in Fig. 77.

It will be found that the candle now burns steadily and brightly.

Now test the direction of the air currents at the mouth of the flask by means of smoking paper. It will be found that air flows down into the flask on one side of the cardboard strip, and up out of the flask on the other side. That is, the neck of the flask is now divided into two passages, one of which serves as an inlet for the air, and the other as an outlet.

It should be noticed in the foregoing experiment that when the inlet and outlet are provided the circulation between the air

in the flask and the outer air is established and maintained by convection. The air, heated by the candle flame, rises and flows upwards out of the flask by the outlet, while fresh air to replace it enters as a downward current by the inlet.

Some of the simpler systems of ventilation depend in this way upon the convection currents produced by heating the air to be circulated at one or more points. The action of a fire and a few Tobin tubes in renewing the air in a room is a familiar example of this method of ventilation. The air heated by the fire ascends the chimney, as outlet, in a steady continuous current, as shown in Fig. 78. This air is replaced by fresh air from outside which enters the Tobin tube A B by a grating in the outer wall at A, and is delivered into the room at some convenient point B.

In this way the air in the room is continually renewed, and if the tube A B is properly placed no draughts are set up in the room.
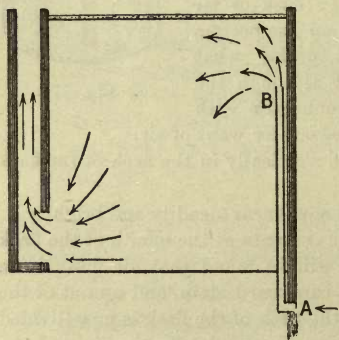
Fig. 78.

Fig. 79.

A window opened in the manner indicated in Fig. 79 is a very satisfactory substitute for a Tobin tube.

71. **Hot-Water Systems of Heating.**—The circulation of water in a system of hot water pipes, as usually arranged for supplying hot water for domestic purposes or for heating a building, is due to convection.

The usual arrangement of the heating system is shown in Fig. 80.

The water heated in the boiler A at the lowest point in the system rises through the outflow pipe ABC to the feed cistern C,
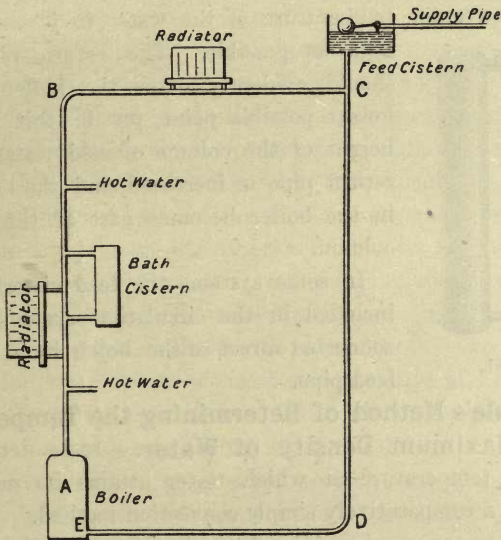
Fig. 80.

at the highest point of the system. This water is replaced in the boiler by a downward flow in the return pipe CDE from the feed cistern. This cistern is supplied from the local water supply by a cock fitted with a ball valve in the usual way.

The efficiency of the system depends upon the difference in pressure at the point E, where the return pipe enters the boiler, due to the column of *hot* water in the outflow system from

E to C by way of AB, and the column of *cold* water in the return
system from C to E by way of D.

This difference of pressure evidently depends upon the differ-
ence between the average density of the water in the outflow
column and the average density in the return column, and is
therefore increased by having the outflow column as hot as
possible, and the return column as cold as possible.

In order that this difference may be as great as possible the
outflow pipe should go as direct as possible to its highest points,
so that the average temperature of the water in it may be as

Fig. 81.

high as possible. The return pipe, too,
should evidently enter the boiler at the
lowest possible point, for in this way the
height of the column of cold water in the
return pipe is increased, and the hot water
in the boiler becomes part of the outflow
column.
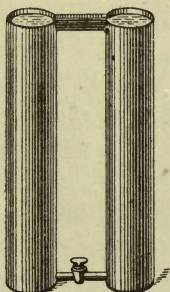
In some systems the feed cistern is not
included in the circulation system, and is
connected direct to the boiler by a separate
feed pipe.

**72. Joule's Method of Determining the Temperature
of the Maximum Density of Water.**—Joule determined
the exact temperature at which water attains its maximum
density by a comparatively simple convection method.

The apparatus employed by Joule is shown in Fig. 81. It
consists, as shown in the figure, of two vertical tubes com-
municating at the bottom by a pipe fitted with a stopcock, and
at the top by a narrow open trough.

The stopcock being closed, the tubes were filled with water at
different temperatures, the temperature in one tube being a little
below 4° C., and that in the other a little above 4° C. The
temperature of the water in the tubes was then adjusted, after
repeated trials, until on opening the stopcock there was *no* flow

of water from one tube to the other. This state of equilibrium between the tubes was indicated by a float, which was placed in the communicating trough connecting the tubes at the top. When any flow took place from one tube to the other through the communicating pipe below, the float in the trough above at once moved in the opposite direction.

When the temperatures are adjusted until no flow takes place, the density of the water in the two tubes must evidently be the same.

It is clear that when one temperature is a little above, and the other a little below the temperature of maximum density, a great many pairs of temperature can be found at which water has the same density, and that the mean temperature of each pair is approximately the temperature of maximum density.

Joule determined, therefore, by experiment, as described above, a number of pairs of temperatures for which no flow took place from one tube to the other, and deduced the temperature of maximum density from the mean values of these pairs.

When the difference between the two temperatures for which no flow takes place is *small*, the mean of the two is almost exactly the temperature of maximum density, and if it were possible to maintain each column at a uniform temperature, and to determine the temperatures of the columns at the exact instant of equilibrium, the method would be a very exact one.

Joule determined the temperature of maximum density of water to be 39·1° F., or 3·95° C.

CHAPTER XII.

THE MECHANICAL EQUIVALENT OF HEAT.

73. Heat is a Form of Energy.—It has already been stated that heat is a form of energy. It is generally assumed to be the molecular kinetic energy which a body possesses in virtue of the vibratory motion of its molecules. It is observed that energy in other forms may be converted into heat, and that work done on a body may produce heat in the body. It is also observed that heat may be converted into other forms of energy, and that it may be expended in doing work.

The heat produced during combustion is the result of the transformation of chemical energy into heat. Thus, when carbon and oxygen combine to form carbon dioxide, the molecular potential energy (chemical energy) of the carbon and the oxygen before combination is greater than the molecular potential energy of the carbon dioxide after combination, and the loss of molecular potential energy which thus takes place during the combination appears as heat during the process of combustion. When a bullet strikes a target, the kinetic energy which it possesses is converted into heat in the bullet. The bullet is flattened on the target, and its kinetic energy is, therefore, expended in doing work in deforming the bullet against opposing molecular forces, and is thereby converted into heat in the bullet.

When a gas is compressed, the mechanical work done during compression is converted into heat in the gas. For example, when a bicycle pump is used in pumping air into a tyre, the

heat developed in the compressed air is communicated to the barrel of the pump, which becomes quite hot. Similarly, when a compressed gas is allowed to expand freely, it does work in making room for itself against external pressure, and expends a considerable quantity of the energy which it possesses as heat in doing this work. This explains why a gas may be cooled to a very low temperature by suddenly reducing the pressure to which it is exposed and allowing it to expand freely.

Heat is expended in doing work in every form of heat engine. The quantity of heat taken in by the working substance at the boiler or source of heat is always greater the quantity given up by the substance in the condenser, and of the difference between these two quantities a proportion which depends upon the efficiency of the engine is converted into work.

The first experiments, which showed that heat could not be a material fluid and which led to the establishment of the theory that heat is a form of energy, were made by Count Rumford in 1798. At this date Count Rumford* was employed by the Bavarian government in boring cannon at Munich. He observed that an enormous quantity of heat was developed in the process of boring, and was led by his observations to experiment with the object of discovering the source of the apparently unlimited supply of heat. He argued that if heat was a material fluid its production could be explained only by some progressive change in the metal of the cannon which greatly reduced its capacity for heat. The only portion of the metal which could be changed in this way was the portion reduced to borings by the boring chisel. Rumford compared the thermal capacity of a quantity of borings with the thermal capacity of an equal quantity of the unchanged metal, and found that the borings had exactly the same capacity as the unchanged metal. He also showed that

* Count Rumford, whose name was Benjamin Thomson, was of English parentage, and was born at Woburn, near Boston, in 1753.

when a blunt chisel which produced a very small mass of borings was used an even greater supply of heat was produced.

As the result of his experiment Count Rumford finally came to the conclusion that heat could not possibly be a material substance, for he says, in summing up his views, " that the heat generated in these experiments appeared to be inexhaustible," and " that anything which any insulated body or system of bodies can continue to furnish without limitation cannot possibly be a material substance."

Davy's experiments about the same date were even more conclusive than Rumford's on this point. Davy showed that when two pieces of ice are rubbed together at a temperature below the melting point, heat is produced and the ice melts. In this case the production of the heat could not be explained by supposing the water produced by the friction to have a smaller capacity for heat than the ice. It was even then a recognised fact that the thermal capacity of water was *greater* than that of ice.

Davy's experiments thus showed that a steady supply of heat could be obtained by rubbing together two pieces of matter which, although they were supposed to be the source of the supply, did not themselves lose heat but actually gained it. This result made it evident that heat could not be a material substance.

It was not, however, until 1840 that it was generally accepted that heat is a form of molecular energy associated with the *motion* of the molecules.

We now know that the true explanation of Rumford's and Davy's experiments lies in the fact that the work done against friction was converted into heat at the point where the work was done, and that so long as work continued to be done, heat continued to be produced.

74. Joule's Experiments.—When it is accepted that heat is a form of energy, it is obvious that when work is done in

producing heat there must be a definite quantitative relation between the amount of work done and the quantity of heat produced. Similarly, when heat is expended in doing work, there must be the same quantitative relation between the heat expended and the work done.
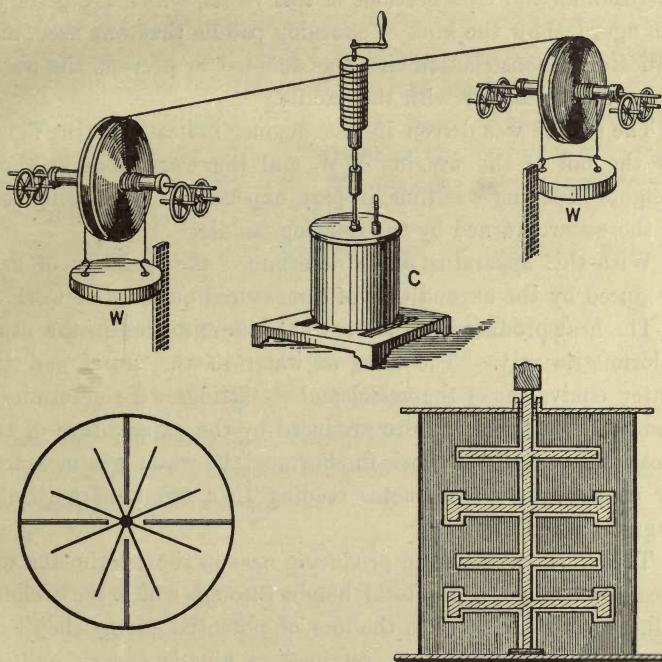
Cross Section of C.   Vertical Section of C.
(Shewing Vanes of Paddle & Partitions)

Fig. 82.—Joule's Apparatus.

During the period 1840 to 1849 Dr. Joule, of Manchester, carried out a very important series of experiments, which finally established the dynamical theory of heat, and determined the equivalent of a calormetric unit of heat in dynamical units of energy.

The best known and most important of Joule's experiments are those in which heat was developed by churning water in a copper vessel which served as a calorimeter. The apparatus employed in these experiments is shown in Fig. 82. The vessel in which the water was churned is shown at C. The longitudinal and cross-sections of this vessel, which are g ven in the figure, show the kind of churning paddle that was used, and indicate the construction that was adopted to prevent the water from rotating bodily with the paddle.

The paddle was driven in the manner indicated in the figure by the fall of the weights WW, and the work done by these weights in falling was thus, in part, expended in generating heat in the water churned by the rotating paddle.

With this apparatus Joule determined the quantity of heat produced by the expenditure of a measured quantity of work.

The heat produced in the vessel C was measured in the usual calorimetric way. The mass of water in the vessel and the water equivalent of the vessel and its fittings were determined, and the rise of temperature produced by the expenditure of the measured quantity of work in churning the water was measured by an accurate thermometer reading to a two-hundredth of a degree Fahrenheit.

The work expended in producing heat in the calorimeter was measured by noting the total height through which the weights fell, and subtracting from the loss of potential energy they thus sustained the energy they retained as kinetic energy, and the work done against friction *outside* the calorimeter.

If W denote the work done in dynamical units and H denote the heat produced in calorimetric units, then $\dfrac{W}{H}$ is the equivalent of one calorimetric unit of heat in dynamical units of work or energy. This equivalent is known as *Joule's equivalent* or *the mechanical equivalent of heat*, and is usually denoted by the letter J. We may, therefore, write

$$\frac{W}{H} = J, \text{ or } W = JH,$$

as the general relation expressing the equivalence between work and heat.

As the mean result of his experiments, Joule found one pound degree (Fahrenheit) of heat—that is, the quantity of heat required to raise one pound of water through one degree Fahrenheit—to be equivalent to 772 foot-pounds of work.

Later determinations of this equivalent show that Joule's result is a little too low. The value given by recent determinations is very nearly 778 foot-pounds per pound-degree Fahrenheit of heat.

This value of J may be expressed in different units as follows :—

$J = 778$ foot-pounds per pound-degree Fahrenheit.

    $= 1,400$ foot-pounds per pound-degree Centigrade.

    $= 4\cdot19 \times 10^7$ ergs per calorie.

When this equivalent is known the quantity of work, W, equivalent to any given quantity of heat, H, can be at once determined by the relation

$$W = JH,$$

where J is given the values appropriate to the units in which W and H are expressed.

CHAPTER XIII.

RADIATION.

75. Nature of Radiation.—Radiation is the wave motion which is set up in the ether at the surface of every body by the vibratory motion of its molecules.

Every body is thus continuously losing heat by the radiation which it emits from its surface. The energy which a body possesses as heat is transformed continuously at its surface into energy of wave motion in the ether, and in this form it travels outwards from the body in all directions into the surrounding ether. The *emission* of radiation by any body is thus a process of transformation of energy from heat in the body into energy of wave motion in the ether, and the extent to which it takes place must depend upon the nature of the surface layer in which the transformation takes place by the action of the vibrating molecules of the body on the adjacent ether.

Every body is also continuously gaining heat by *absorbing* some of the radiation incident upon it from surrounding bodies. Some of the energy of the incident wave motion is in general expended in increasing the vibratory energy of the surface layer of molecules on which it is incident, and thus appears as heat in the body. The *absorption* of radiation by a body is thus a process of transformation of energy which is exactly the reverse of that which takes place in the emission of radiation, and the extent to which it takes place must evidently depend in the same way as emission does upon the nature of the surface layer in which the transformation takes place.

If a body gains heat by the absorption of incident radiation at the same rate as it loses it by emission of radiation its temperature remains constant. If, however, it gains heat more rapidly by absorption than it loses it by emission its temperature rises, and if it loses heat more rapidly by emission than it gains it by absorption its temperature falls.

It will be seen from what has been said that heat may be transferred from one body to another by radiation, for the radiation emitted by the one body may be absorbed by the other. Heat thus passes from one body to the other, but it is specially important to notice that it travels through the space between the bodies *not* as heat in the intervening material medium, but *as energy of wave motion in the intervening ether*. Thus heat from the sun reaches the earth by radiation. The radiation emitted by the sun travels through the intervening ether, and is absorbed or transformed into heat at the surface of the earth. The atmosphere cannot, therefore, be heated directly by radiation from the sun, for the radiation passes through the ether which permeates the atmosphere as energy of wave motion, and cannot, therefore, appear as heat in the air. The atmosphere is heated from the surface of the earth by convection, and also to a small extent, as explained below, by absorption of the solar radiation as it passes through the ether in the air.

Similarly, when a person stands before the fire the heat from the fire reaches him by radiation through the intervening ether and does not heat the intervening air which takes no part in the process, except in so far as the relation between the air molecules and the adjacent ether leads to some slight absorption of the radiation of the air.

76. Radiation and Temperature.—The radiation which a body emits changes in character and in quantity as the temperature of the body rises.

The wave motion in the ether which constitutes the radiation

emitted by any body is always of a very complex type.* As the temperature rises it becomes more and more complex by the addition of new constituents of shorter and shorter wave length. The constituents added as the temperature rises from a low red heat to a white heat have the special property of affecting the retina of the eye and producing the sensation of sight. These constituents which lie within a certain range of wave length †️ are called *light*, and differ only in their special power of exciting the optic nerve from the general body of radiation emitted by the body.

It thus appears that a body at a given temperature should emit radiation of a definite type containing all the constituents appropriate to the temperature. It is found, however, that no body emits the full radiation appropriate to its temperature. There are always in every case certain constituents wanting, so that the character of the radiation emitted by a body at any temperature depends not only on the temperature but also upon the body itself. It thus happens that the type of radiation emitted by a body may be characteristic of the material of the body or of the material of its surface layer.

The quantity of radiation emitted by a body—that is, the rate at which a body loses heat by radiation—increases rapidly with the temperature. The intensity of each constituent already acquired increases, and new constituents are added as the temperature rises, so that the energy radiated by the body must increase as the temperature rises.

It has been shown from theoretical grounds, and also by experiment, that the rate at which a body emits heat by radiation at any temperature is, **in the case of a body which emits the full radiation appropriate to the temperature,** directly proportional to the fourth power of the absolute temperature of the body. This law was first stated by Stefan, and is known as *Stefan's law*.

77. Transmission of Radiation through Material Media.

—When radiation passes through the ether in any material some portion of the energy of the wave motion in the ether is communicated to the molecules of the medium and appears as heat in the medium. That is, some portion of the radiation energy transmitted through the ether in a material medium is absorbed by the medium during transmission.

The amount of radiation energy absorbed in this way during transmission through any medium varies very widely with the medium. Some media, such as dry air and other gases, absorb very little, and are, therefore, very slightly heated by the transmission of radiation through them.* Other substances absorb such a considerable proportion of the radiation passing through them * that a given flow of radiation may be completely absorbed by a comparatively small thickness of the substance, and may, therefore, be unable to penetrate to any great depth or to travel through any appreciable thickness of the substance.

In the case of other substances the radiation incident on its surface is at once absorbed completely by the surface layer, and cannot be said to penetrate to any depth in the substance.

It is found, too, that a medium which allows radiation to pass through it generally absorbs different constituents of the radiation to different extents. The extent to which a medium absorbs the radiation transmitted through it may thus depend upon the character of the radiation under transmission—that is, upon the nature and temperature of the source of the radiation.

Thus, glass which transmits the constituents of radiation which constitute *light*, almost completely absorbs the radiation emitted by a body below a red heat. This explains the use of glass in glass-houses; a large proportion of the radiation from the sun (chiefly those constituents which belong to temperatures between a red heat and a white heat) passes through the glass and is absorbed by the objects within the house. These objects

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* That is, through the ether which permeates them.

thus become heated, but the radiation which they emit cannot escape from the house, for it is absorbed by the glass. The house thus becomes an enclosure, of which the walls and the objects in it are steadily gaining heat. The temperature reaches a maximum when the house loses heat to the ground and the outer air at the same rate as it gains it.

In the same way a sheet of glass forms an effective fire screen. The light rays pass through the screen, but a sufficient proportion of the radiation is absorbed to moderate the heating effect of the full radiation from the fire. Water vapour behaves in much the same way as glass, and water vapour in the air has, to a less extent, the same effect as the glass covering of a glass-house.

A solution of alum in water, although quite transparent to light, absorbs the radiation from a body below a red heat even more strongly than glass. Rock salt, on the other hand, is transparent to light, and also in an equal degree to radiation from bodies below a red heat. A solution of iodine in carbon bisulphide is an example of a substance which is opaque to light, but very transparent to low temperature radiation.

78. **Effect of the Surface of a Body on the Emission and Absorption of Radiation.**—When a body at any temperature cools in air, or in any gas in an enclosure at a lower temperature than the body, the cooling is due to conduction and convection as well as to radiation. When, however, a body cools in a vacuum, the cooling is entirely due to radiation. The body loses heat by the radiation which it emits, and gains heat by the radiation which it absorbs. Hence, by experimenting on the cooling of a body in a vacuum, it can be shown that the rate at which a body loses heat by radiation depends upon

(a) The temperature of the body ; for this determines the rate at which it loses heat by the radiation which it emits.

(b) The temperature of the walls of the enclosure in which it cools ; for this determines the rate at which the body gains heat

by the absorption of radiation from the enclosure walls. The body evidently gains the same amount of heat by absorption as it would emit at the temperature of the enclosure, for if it were at the temperature of the enclosure it would receive the same amount as it emitted.

(c) The nature of the surface of the body; for this affects the rate at which it emits heat, and also, in the same way, the rate at which it absorbs heat.

The influence of the nature of the surface on the emission and absorption of radiation may be exhibited without experimenting on cooling in a vacuum. When a liquid in a thin vessel of good conducting material cools through a given range of temperature in air in an enclosure of constant temperature, the rate at which it loses heat is found to vary with the nature of the surface of the vessel. This variation can be caused only by the influence of the nature of the surface on the emission and absorption of radiation by the cooling system, for all the other effects which contribute to cooling are practically independent of the nature of the surface of the vessel.

Experiment 100.—Set up the apparatus shown in Fig. 83 for the purpose of comparing the effect of different surfaces on the rate at which a body loses heat by radiation in an enclosure at a constant temperature.

A small flask of thin silver or copper is suspended in the manner shown in the figure, inside the double-walled copper vessel B. This vessel has the space between the walls filled with water, and when covered with the cork cover, C, from which the flask is suspended, forms an enclosure which is maintained by the water jacket at a temperature which is practically constant.

Fill the flask with water at about 60° C., and insert the thermometer, T, and the stirrer, S, as shown in the figure.

Then, in successive experiments note the time taken by the flask and its contents in cooling from 50° C. to 40° C. When the surface of the flask is

(a) Brightly polished.
(b) White-washed.
(c) Blackleaded.

(d) Painted a dead black with a paint made with lampblack and shellac varnish.

(e) Covered with a fine coating of soot from a smoky flame, such as is obtained by burning a small piece of camphor.

It will be found that the time taken is greatest in case (a), and least in cases (d) and (e), which should be about equal. The cases (b) and (c) should give intermediate values, greater for (b) than for (c).

This shows that a brightly-polished surface emits radiation at a very low rate, and is therefore said to be a bad radiating surface. A dead black surface, or a lampblack surface, on the other hand, emits radiation at a high rate, and is a good radiating surface. Experiment shows that it is, in fact, the best radiating surface.
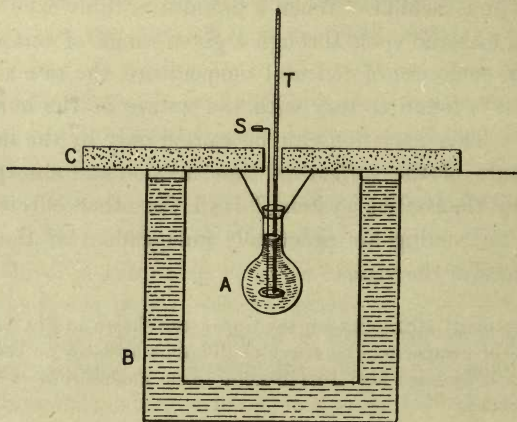
Fig. 83.

Now, rearrange the experiment, and put hot water, at any convenient temperature, in the outer jacket, and water at the ordinary temperature in the flask. Then, in successive experiments, as before, note the time taken by the flask and its contents in heating from, say, 15° C. to 25° C., when the surface of the flask is varied as described at (a), (b), (c), (d), and (e) above.

It will be found that the times taken in the five cases are not only in the same order as before, but also in the same ratio. This shows that the nature of the surface affects its power of absorbing radiation in exactly the same way as its power of emitting radiation, and that a surface which is a good or bad radiating surface is also in the same degree a good or bad absorbing surface.

It should be noted that a highly-polished metal surface is a very bad radiating and absorbing surface, and that a dead black lamp-black surface is the best radiating and absorbing surface.

The influence of surface condition on the emission and absorption of radiation, indicated by these experiments, could in some measure be predicted from theoretical considerations. Radiation, it must be remembered, is *wave motion* in the ether, so that when radiation is incident on the surface of any body it is, in general,* partly reflected (regularly and irregularly) at the surface, partly absorbed at the surface, and, it may be partly transmitted on into the ether in the substance of the body. In the case of a highly-polished surface, practically all the incident radiation is regularly reflected at the surface, and a very small proportion is absorbed. A highly-polished surface must, therefore, be a very bad absorbing surface, and since absorption and emission are merely reverse aspects of the same process, it must also be a very bad radiating surface.

Similarly, a surface covered with finely divided whiting diffuses or irregularly reflects a considerable proportion of the incident radiation, and is therefore only a moderately good radiating and absorbing surface.

A lampblack surface, on the other hand, absorbs practically all the radiation incident on it, and its radiating and absorbing power at any temperature are, therefore, very nearly of the highest value possible at that temperature.

It should be noted, too, that when the radiation emitted by any body is lacking in certain constituents appropriate to the temperature, the surface of the body, since it does not emit these constituents, will not absorb them when they are present in the radiation incident on the body. This power of *selective* emission and absorption which a surface possesses for radiation in general is the same as that which gives rise to surface colours for *light* radiation, and is the cause of great and apparently

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* See *Sound*, chap. vi., and *Light*, chap. i.

inexplicable variety in the absorbing and radiating powers of different surface for the same radiation, and also of the same surface for radiation from different sources.

It is found that a lampblack surface absorbs practically the whole of the radiation incident on it, whatever the type of the radiation may be. It is, therefore, a surface which, at any temperature, emits very nearly the *full* radiation appropriate to the temperature. The radiation from a lampblack surface at any temperature may, therefore, be taken as directly proportional to the fourth power of the absolute temperature, in accord with Stefan's law.

79. **Determination of the Specific Heat of a Liquid by the Method of Cooling.**—The specific heat of a liquid may be determined conveniently by the method of Exp. 100, with the apparatus shown in Fig. 83. It is plain from what has been said that if the small flask is filled successively to the same point with a number of different liquids and allowed to cool in each case through the same range of temperature, and under exactly similar external conditions, it must lose heat at exactly the same rate in each case.

Hence, if the flask when filled with M grammes of *water* cools through $\theta°$ in t seconds, the rate at which it loses heat per second is given by

$$\frac{M\theta + ms\theta}{t},$$

where m denotes the mass of the flask and s the specific heat of its material.

Similarly, if the flask when filled to the same extent with M′ grammes of *the liquid whose specific heat is to be determined* cools through the same $\theta°$ in $t′$ seconds, the rate at which it loses heat per second is given by

$$\frac{M'x\theta + ms\theta}{t'},$$

where x denotes the specific heat of the liquid.

Since the flask loses heat at exactly the same rate in each case, we have

$$\frac{M\theta + ms\theta}{t} = \frac{M'x\theta + ms\theta}{t'}.$$

That is,

$$(M + ms)\, t' = (M'x + ms)\, t,$$

and in this relation all the quantities are known except the quantity x which is to be determined.

If the flask is light and of fairly large capacity the value of ms will be comparatively small, and the relation given above reduces to

$$\frac{M}{t} = \frac{M'x}{t'}$$

or

$$Mt' = M'xt$$

and

$$x = \frac{Mt'}{M't}.$$

Since the volumes of the two masses of liquid are equal the ratio M/M' is equal to d/d', where d and d' denote the density of water and the liquid respectively. Hence, we may write:

$$x = \frac{dt'}{d't}, \text{ or } x = \frac{t'}{\delta t},$$

where δ denotes the specific gravity of the liquid.

Numerical Example.—In an experiment by this method for the determination of specific heat of aniline it is found that 102 grammes of aniline in the flask cool from 40° C. to 35° C. in 8 minutes 10 seconds, while 100 grammes of water in the same flask cool through the same range of temperature, under exactly the same external conditions, in 16 minutes 22 seconds.

The flask is of copper (specific heat ·093) and weighs 12·2 grammes.

In this case the rate at which heat is lost by the water and the flask is:

$$\frac{(100 \times 5) + (12\cdot2 \times \cdot093 \times 5)}{982} \text{ calories per second,}$$

or ·515 calorie per second.

And the rate at which heat is lost by the aniline and the flask is :

$$\frac{(102 \times x \times 5) + (12 \cdot 2 \times \cdot 093 \times 5)}{490} \text{ calories per second,}$$

or $\qquad (1 \cdot 041 x + \cdot 012)$ calories per second.

Hence, we have

$$1 \cdot 041 x + \cdot 012 = \cdot 515,$$

or $\qquad\qquad 1 \cdot 041 x = \cdot 503,$

and, therefore, $\qquad x = \dfrac{\cdot 503}{1 \cdot 041} = \cdot 484.$

That is, the specific heat of aniline is given by the experiment as ·484.

If we take the approximate formula :

$$x = \frac{\mathrm{M}}{\mathrm{M'}} \cdot \frac{t'}{t}.$$

or $\qquad\qquad x = \dfrac{t'}{\delta t}, \text{ we get}$

$$x = \frac{490}{1 \cdot 02 \times 982} = \cdot 49.$$

The accuracy of the method is improved by using a flask with a very highly polished surface, for the time taken in cooling through a given range of temperature is thus increased, and can, therefore, be more accurately determined.

80. **Newton's Law of Cooling.**—The rate at which a body cools under the condition of Exp. 100 is found to depend upon the excess of its temperature above the temperature of its surroundings. The greater the excess the greater the rate of cooling. Newton stated that the rate of cooling was directly proportional to the excess of temperature. The truth of this statement can be tested by the following experiment.

Experiment 101.—Set up the apparatus of Exp. 100, fill the jacket vessel with water at the ordinary temperature and the flask with water at about 70° C.

Then allow the flask to cool to the temperature of the surrounding jacket, and record its temperature as indicated by the thermometer in it at intervals of one minute during the cooling. The water in the flask should be stirred before taking each reading. From the record of temperatures thus obtained the *fall of temperature* which takes place in each minute during the cooling can be calculated. The fall of

temperature in any minute interval gives the *rate* of fall of temperature per minute corresponding to an excess of temperature which may be taken as the excess of the average temperature of the water during the minute interval over the temperature of the water jacket surrounding it. Thus, if the temperature of the water jacket is 14° C., and the water in the flask cools from 35·6° C. to 34·4° C. in a given minute, the rate of cooling of the water is 1·2 degrees Centigrade for an excess of (35 – 14) or 21 degrees.

From the results obtained in this way plot a curve showing how the rate of cooling* varies with the excess of temperature.

It will be found that the curve has the form shown in Fig. 84.

It can be seen at once from the form of this curve that Newton's statement is approximately true only when the excess
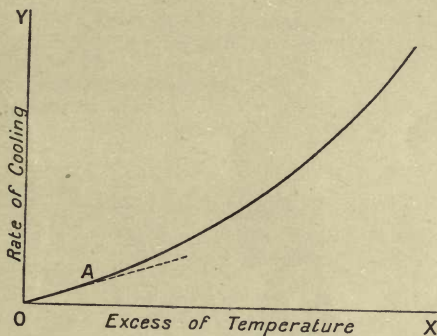
Fig. 84.

of temperature is small. If it were true generally the curve in the figure should be a straight line. The curve, however, is concave upwards, showing that the increments in the rate of cooling for equal increments in the excess are not constant (as required by a proportional law) but increasing.

A short length of the curve from the origin to some point A where the excess is comparatively small is approximately

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* The *rate of cooling* of a body is usually taken to mean the rate of fall of *temperature*. For any given body (of constant specific heat), however, it is directly proportional to the rate of loss of *heat* by the body, and may be taken as indicative of that loss.

straight, and shows that for small excesses of the temperature of a body above the temperature of its surroundings the rate of cooling of the body is directly proportional to the excess of temperature. This limited relation between rate of cooling and excess of temperature is known as *Newton's law of cooling*.

INDEX.